Dissolved Oxygen and Temperature Profiles for the Central Basin of Lake Erie Quality Assurance Project Plan

Appendix D

Revision 03, January 2007

DISSOLVED OXYGEN AND TEMPERATURE PROFILES
for the
CENTRAL BASIN OF LAKE ERIE

QUALITY ASSURANCE PROJECT PLAN

January 2007

U.S. Environmental Protection Agency
Great Lakes National Program Office
77 West Jackson Boulevard
Chicago, Illinois 60604

REVISION: 03

APPROVED   DATE

Paul Bertram
Project Leader, Monitoring and Information Branch   _____

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Project Management

A1   Distribution List

This QAPP and subsequent revisions shall be distributed to:

Project Leader: Paul Bertram, GLNPO
Quality Assurance Officer: Louis Blume, GLNPO
R/V Lake Guardian: Marine Technician
Project Field Personnel: Survey Chief Scientist

A2   Project Organization

This project is being conducted by the U.S. Environmental Protection Agency, Great Lakes National
Program Office, Chicago, Illinois, as part of its annual program to monitor the status of the open waters
of the Great Lakes.

Project Leader: Paul Bertram is responsible for participants adhering to the requirements of the QAPP,
and for overall data quality and accuracy.

Ship operations and scheduling: George Ison will coordinate ship operations in his capacity as Contract
Officer Representative.

Sampling operations: Paul Bertram or his appointed representative(s) will conduct the sampling
operations with assistance from the ship contractor or other qualified personnel.

Laboratory operations: Paul Bertram or his appointed representative(s) will conduct or oversee onboard
laboratory procedures with assistance from ship contractor or other qualified personnel.

Data reduction and analysis: Paul Bertram will conduct or oversee data reduction, analysis and reporting

A3   Problem Definition and Background

Lake Erie has been severely impacted by excessive anthropogenic loadings of phosphorous resulting in
abundant algal growth and dissolved oxygen depletion in the hypolimnion of the Central Basin.
However, reductions in total phosphorous loadings and concentrations in the water column have been
observed since their peak in the late 1960's and early 1970's. Models predict that a loading of
phosphorous to Lake Erie of no more than 11,000 tonnes/year should be reflected by average Central
Basin concentrations of 10 µg/liter, and should allow 90% of the bottom waters of the Central Basin to
remain aerobic all year.

In response to the Great Lakes Water Quality Agreement of 1978 (GLWQA) between Canada and the
U.S., phosphorous reduction programs were implemented. These programs have been largely
successful. Annual loadings of phosphorous to Lake Erie are presently near the targeted 11,000 tonnes,

and elimination of anoxia in the hypolimnetic waters in the Central Basin is anticipated, coinciding with observed reductions in total phosphorous concentrations.

To determine if "restoration of year-round aerobic conditions in the bottom waters of the Central Basin of Lake Erie" (GLWQA) has been achieved, annual monitoring of the water column for thermal structure and dissolved oxygen concentrations are needed throughout the stratified season. These data are also required to calculate the normalized dissolved oxygen depletion rate, allowing direct comparison of one year's dissolved oxygen history with previous years, despite differences in weather patterns and subsequent thermal structure.

The monitoring program described by this Quality Assurance Program Plan is designed to provide the necessary data to observe dissolved oxygen concentrations and to calculate an annual normalized rate of dissolved oxygen depletion in the Central Basin of Lake Erie. These data will be useful to federal and state water quality agencies to assess the effectiveness of phosphorous load reduction programs, and they will be useful to state fisheries agencies to assess the potential impairment to the fishery from anoxic waters.

A4   Project Description

Project Summary

This project is designed to measure the dissolved oxygen and temperature profiles from the surface to the bottom of the water column in the Central Basin of Lake Erie throughout the period of thermal stratification. The rate of oxygen depletion in the hypolimnion will be calculated from repeated measurements of dissolved oxygen concentration and water temperature from early June to mid-September.

The sampling strategy utilized has been defined by the Great Lakes International Surveillance Plan (GLISP, Revised 1986) as developed by the Lake Erie Task Force (LETF) for the Surveillance Work Group of the Great Lakes Water Quality Board of the International Joint Commission. Analyses by the LETF of historic monitoring data for the Central Basin identified the "relatively homogeneous" area from which samples should be taken, and the sampling protocols which would ensure the data to be adequate for monitoring annual dissolved oxygen concentrations and rate of depletion. Therefore, the data collected in this project will fully meet requirements of their intended use.

Utilization of this standardized data collection procedure will also ensure direct comparability of the data collected with those from previous years. Since 1983, this procedure has been successfully employed with minor variations by Ohio State University (1983-1986), U.S. Fish and Wildlife Service (1987-1990) and U.S. EPA Great Lakes National Program Office (1991-1993, 1997-1999, 2001-2006). The data are consistent with other historical measurements dating to 1970, and provide a reliable basis for evaluating long term trends.

Research Vessel

The U.S. EPA *R/V Lake Guardian* will be used as the sampling platform whenever schedules and other operating constraints so permit. The ship's crew are familiar with both the program and the operation of the equipment to ensure careful deployment of the instruments and accurate positioning on the stations. In the event that the *R/V Lake Guardian* is not available for one or more of the scheduled sampling times, alternative vessel support will be obtained with adequate navigational aids and equipment for deployment of sampling gear to conduct the sampling operation with no loss in accuracy or precision of the data.

Sampling Procedure Summary

Ten sites in the relatively homogeneous area of the Central Basin (see locations listed in Section B1 and the map in Attachment 1) will be visited on each of six occasions, separated by approximately 3-week intervals. Sampling times include early and late June, mid-July, early and late August, and mid-September. At each station visit, the thermal structure of the water column is recorded by an electronic CTD (conductivity, temperature, depth) computerized data recording module (SeaBird Electronic, Inc.). Dissolved oxygen (DO) concentrations are measured and recorded by a sensor integrated with the CTD instrument package. Readings are obtained 4 times per second to provide a nearly continuous profile from the top to the bottom of the water column. The accuracy of the dissolved oxygen readings is confirmed by collecting water samples from both the epilimnion and hypolimnion in a Niskin bottle and performing dissolved oxygen concentration measurements of the collected water by the Winkler (wet lab) method (see Attachment 3, *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*).

Ancillary Data Collection Summary

Ancillary data useful to the interpretation of the dissolved oxygen and temperature profiles will also be collected. Included, as appropriate, are total phosphorous, Secchi disk depth, air temperature, wind direction and speed, wave direction and height, barometric pressure and ambient precipitation. Data quality objectives and analytical protocols for total phosphorous analysis are included in the QAPP for the GLNPO annual water quality monitoring survey, *Quality Assurance Project Plan, Great Lakes Survey Studies of Lakes Michigan, Huron, Erie, Ontario and Superior*. Data quality objectives for the other measurements are within instrument error and professional judgement of the observer.

Required Records and Reports

All data collected in the field will be entered onto a field data sheet (see Attachment 2, *Dissolved Oxygen Survey – Lake Erie Central Basin Dissolved Oxygen Data (Winkler)*) unique to each station visit. Electronic files obtained from the SeaBird instrumentation cluster will be duplicated on site and stored in multiple locations (e.g., hard disk and portable memory devices). All QA/QC data associated with a station visit will be recorded on the field data sheet or attached to the sheet for convenient audit.

At the end of the field season, all necessary data will be combined into an electronic format, and the normalized rate of dissolved oxygen depletion will be calculated. Results will be made publically available via GLNPO web site, printed report, GPRA report, or other distribution method.

A5   Data Quality Objectives for Measurement Data

Data Quality Statement

A true reference standard for performance of accuracy measurements for dissolved oxygen cannot be obtained. However, the Winkler titration method for determination of dissolved oxygen in water samples theoretically provides an accurate stoichiometric surrogate measurement. Electronic sensors (DO probes) are deployed to increase the resolution of dissolved oxygen profiles in the water column, but their output values are compared to independent Winkler measurements for calibration and control checks. Therefore, based on comparisons with Winkler titrations:

> *Dissolved oxygen concentrations will be determined by electronic sensors within an accuracy of 10% at values greater than or equal to 5 mg/L and within 0.5 mg/L at values less than 5 mg/L at a confidence level of 95% at each deployment of the instrument.*

Over the course of the project, average relative differences will be within 5% at values greater than 5 mg/L, and within 0.4 mg/L at values less than 5 mg/L.

Similarly, accuracy of temperature measurements from electronic probes is evaluated with respect to an independent temperature sensor, e.g., electronic thermister. Surface water temperature will be determined within 2% of thermometer readings at a confidence level of 95%.

Rationale

The overall quality assurance objective for this project is to acquire accurate measurements of oxygen and temperature profiles at Central Basin stations in Lake Erie that are representative of actual conditions at the time of sampling. Measurements must be sufficiently precise and representative of conditions at all depth strata to allow for accurate computation of oxygen depletion rates that are comparable with previously acquired data used in long-term trend analysis.

The criteria for acceptable accuracy and precision for this project are based on 1) Relative Percent Differences (RPD) between two independently derived measurements, or 2) estimated obtainable precision as indicated by previous survey data. The RPD is defined as the difference between two measurements divided by the average of both and expressed as a percentage. The RPD values for accuracy are determined from independent measurements taken at or near the surface of the water column and in the hypolimnion 1 meter off the bottom. The RPD values for precision are determined from independent SeaBird profiles expressed as an integrated average of hypolimnionic and epilimnionic waters (see B10: Data Management: Calculation of Dissloved Oxygen Depletion Rate).

At the surface, exact location of the instrument probe and the water sampling bottles is controllable, and oxygen concentrations are usually near saturation. Under these circumstances, dual measurements of oxygen are representative of that stratum and RPDs are a good indicator of accuracy.

In the hypolimnion, two factors confound the RPD statistic. 1) In cases when the hypolimnion is 3 meters or less thick and surface wave heights are 1 meter or more, accurate positioning of the water

collection bottle is sometimes difficult, and entrainment of more highly oxygenated water from the thermocline or even the epilimnion is possible. The resultant Winkler determination of dissolved oxygen may then be greater than is representative of the hypolimnion. 2) As absolute dissolved oxygen concentrations decrease in the hypolimnion, progressively smaller differences in independent measurements are reflected by correspondingly larger RPDs. Therefore, acceptable accuracy for dissolved oxygen may also be defined in terms of absolute differences between independent measurements.

Accuracy

Accuracy is a measure of agreement between a measurement (or an average of measurements of the same thing), and the amount actually present. The following data comparisons will be applied to the stated acceptable limits to determine the accuracy of dissolved oxygen and temperature measurements. Measured values will be well above instrument or method detection limits.

Dissolved Oxygen	a) Surface	A lake basin average RPD of 10% or less between Winkler DO measurements and probe values for surface water.
		and
	b) B-1	A lake basin average RPD of 10% or less between Winkler DO measurements and probe values for waters 1 meter off the bottom when the DO concentrations are at least 5 mg/L, or an absolute difference between measurement methods of 0.5 mg/L or less when DO concentrations are less than 5 mg/L. When sampling constraints restrict reliable collection of bottom waters for Winkler determinations (see Section 5.1), the RPD for surface samples will confirm the accuracy of SeaBird values.
Temperature		An RPD of 2% or less between manual thermometer readings of surface water and the SeaBird values from the same depth.

Precision

A measure of mutual agreement among multiple measurements of the same property. Precision will be evaluated to determine if measurement methods are being conducted in a consistent manner. The following comparisons will be compared to the stated precision limits to evaluate measurement consistency.

Dissolved Oxygen	An RPD of 5% or less between probe replicate measurements as determined every five (5) stations, or once/day, whichever is more frequent
	and

Absolute difference between any replicate Winkler measurements of 0.2 mg O_2/L or less.

Temperature   An RPD of 2% or less between SeaBird replicate measurements, as determined every five (5) stations, or once/day, whichever is more frequent.

Completeness

For this QAPP, completeness is the measure of the number of samples obtained compared to the amount that was expected to be obtained under normal conditions. The completeness goal is to obtain dissolved oxygen and temperature profiles within accuracy and precision limits at 90% of all designated stations during each survey. At each station visit, at least 90% of all planned ancillary data will also be recorded.

Representativeness

Data from historic surveys performed under similar sampling designs have been shown to be representative of conditions in the Central Basin of Lake Erie. Audits of accuracy and precision limits will ensure that representative values are obtained during this survey. Particular attention will be paid to samples within the hypolimnion when dissolved oxygen concentrations fall below 5 mg/L.

Comparability

The comparability of data from this project with previous data is maintained by implementing the same sample design and similar data collection procedures. The project design and sampling procedures being used follow the recommended procedures from the GLISP in order to ensure comparability of data with historic surveys.

Summary table

The following table displays a summary of quality assurance objectives for this project.

Parameter/Reporting Units	Sample Type	Frequency	Acceptance Criteria
SeaBird Dissolved Oxygen, mg O_2/L Precision	Probe Replicate	1 per 5 stations	within 5% agreement
Accuracy	Method Comparison SeaBird versus Winkler	Two per station	$\leq$ 10% RPD or difference $\leq$ 0.5 mg O_2/L (goal per station; acceptance criteria per survey)
Resolution	Probe specs	NA	0.02 mg/L
Completeness	Routine	NA	90% all stations 100% profiles each station
Winkler Dissolved Oxygen, mg O_2/L Precision	Winkler Replicates	All Surface and B-1 samples	Absolute difference $\leq$ 0.2 mg/L
Accuracy	Method Comparison SeaBird versus Winkler	Two per station	$\leq$ 10% RPD or difference $\leq$ 0.5 mg O_2/L (goal per station; acceptance criteria per survey)
Resolution	Method precision spec	NA	0.2 mg/L 90% all stations
Completeness	Routine	NA	95% analyses planned

SeaBird Temperature, C			
Precision	Probe Replicate	1 per 5 stations	≤ 2% RPD
Accuracy	Method Comparison SeaBird versus Thermometer	One per station	≤ 2% RPD
Resolution	Instrument specs	NA	0.0005 C
Completeness	Routine	NA	90% all stations 100% profiles each station

A6   Special Training Requirements

Operation of the SeaBird CTD cluster and Rosette water sampling device requires familiarity with the hardware and with the computer software that controls their function. The software is Microsoft Windows compatible, and it prompts for required entries through a graphics user interface (GUI).

Laboratory analysis of dissolved oxygen by Winkler titration requires good standard laboratory practices and familiarity with the methodology.

When personnel other than the Project Leader conduct sampling and laboratory operations, the Project Leader will provide or arrange for the necessary training and will conduct a post-survey audit of the sampling and laboratory operations for adherence to the QC protocols to ensure data quality objectives have been met.

A7   Documentation and Record

All data will be acquired and recorded during each station visit or before the end of each survey. Only the laboratory analyses for total phosphorous will require post-survey activity, and those data should be returned to the Project Leader within 90-days of sample receipt at the laboratory.

Data Reports will include the following information:

- For each station visit: date sampled, epilimnion and hypolimnion average temperature, dissolved oxygen concentration, and total phosphorous concentration (when sampled); hypolimnion thickness, bottom depth, and Secchi depth (when sampled).

- For each survey: QA summary statistics (completeness, average accuracy and precision RPDs, QA narrative assessment of data quality, data caveats), and average hypolimnion dissolved oxygen concentration.

- At the end of the field season: the normalized rate of dissolved oxygen depletion, percentage areal extent of anoxic zone, and narrative of dissolved oxygen findings compared to those of previous years and/or management expectations.

The data reports have no intrinsic expiration time and should be retained in GLNPO files indefinitely. Field data sheets may be destroyed after three (3) years if all the data have been entered into an electronic database and confirmed to be accurately recorded.

Measurement/Data Acquisition

B1   Sampling Process Designs (Experimental Design)

Sampling Strategy

The sampling strategy for this project has been defined in GLISP and is based on the summer thermal structure which is characteristic of the Lake Erie Central Basin. Dissolved oxygen and water temperature measurements will be recorded at ten (10) sampling stations (see Attachment 1, *Dissolved Oxygen Survey Stations Lake Erie Central Basin*) at approximately 3-week intervals from early June through mid-September. Surveys will be conducted in early June, late June, mid-July, early August, late August and mid-September. Each station will be visited once during each survey. All stations will be visited within as short a time interval as possible, generally 2-days, but no more than 4-days apart during each survey.

Sampling Locations

The ten Lake Erie Central Basin stations to be sampled are located at the latitude and longitude positions listed below.

Station #	Latitude	Longitude	Approximate Depth
43	41.78833	-81.94500	23
42	41.96500	-82.04167	22
73	41.97778	-81.75694	24
36	41.93500	-81.47833	23
37	42.11000	-81.57500	24
38	42.28167	-81.67167	22
78	42.11667	-81.25000	23
32	42.08167	-81.01167	22
31	42.25333	-81.10667	21
30	42.43000	-81.20500	21

Sampling Depths

The SeaBird instrument cluster records a nearly continuous profile of temperature and dissolved oxygen from the surface of the water to near the bottom. These profiles provide a visual display of the thermal structure and oxygen content of the water. Historically, data from six (6) depths were used in the calculation of the dissolved oxygen depletion rate. These six depths include:

Thermal Structure	Code	Position
Surface	SURF	1 meter below the surface
Mid-epilimnion	2EPI	middle of epilimnion

Lower epilimnion	3EPI	1 meter above knee of thermocline
Upper hypolimnion	1HYP	1 meter below knee of thermocline
Mid-hypolimnion	2HYP	middle of hypolimnion
Lower hypolimnion	B-1	1 meter above the bottom

The values for temperature and dissolved oxygen at these depths are obtained from SeaBird data files, averaged to 0.5 meter intervals. Exceptions to this sampling strategy may occur if the hypolimnion is 3 meters or less thick, in which case data for the B-1 depth will be obtained, but one or more preceding depths may be eliminated, depending upon configuration and occurrence of the thermocline.

An alternate method for calculating the dissolved oxygen depletion rate was introduced in 2005. This technique incorporated the usage of the entire water profile by integrating the continuous temperature and dissolved oxygen profiles.

Water Samples for Winkler Dissolved Oxygen Titrations

Water samples will be collected by Niskin bottle at the surface and at 1 meter above the bottom at each station visit for determination of dissolved oxygen by the Winkler method. This procedure is performed to confirm the accuracy of the SeaBird sensor measurements. The Niskin bottle may be incorporated into a Rosette sampling system (on the *R/V Lake Guardian*), or it may by attached as a "hand line" on a winch cable (alternate vessel). Replicate measurements of dissolved oxygen concentration will be determined for both depths by the Winkler titration method (*Standard Methods for the Examination of Water and Wastewater,* Sixteenth edition, 1985), as modified for use by GLNPO (see Attachment 3, *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*).

Surface Temperature

Surface water temperature will be measured to the nearest 0.01°C with an electronic thermometer referenced to an NBS standard, by manually inserting the thermometer into water captured by a Niskin bottle immediately after the bottle has been recovered onboard. This procedure is performed to check the accuracy of the SeaBird probe measurements for temperature.

Samples for Total Phosphorous

In addition to dissolved oxygen and temperature profile data acquisition at each station, water samples may be collected for later analysis of total phosphorous. During surveys designated by the Project Leader, a water sample from each of the 6-named depths will be collected by Niskin bottle, and a sample will be transferred to a 125 mL pre-labeled plastic bottle. Each sample will be preserved with 0.4 mL of H_2SO_4 stock (310 mL concentrated acid diluted to one liter). One additional sample from a depth that is pre-assigned at random will be independently collected as a field duplicate. One field blank (distilled or deionized water) will be collected and preserved at each station. All samples will be analyzed for total phosphorous by a contract laboratory using

methods described in the *Quality Assurance Project Plan, Great Lakes Survey Studies of Lakes Michigan, Huron, Erie, Ontario and Superior.*

The sample bottle label will contain the following information: Sample number (i.e., 99GB12S01), Lake Erie, Station number, survey date, preservation used, and parameter to be measured (total phosphorous).

Secchi depth

At each station sampled in daylight hours, the Secchi depth will be determined by manual deployment of the Secchi disk attached to measured line. The depth at which the white disk is just no longer visible is the measured depth. The observation will be recorded on the station log sheet. This is a non-critical, but useful, measurement.

Weather data

At each station, weather and sea state conditions will be recorded, including air temperature, wind direction and speed, wave direction and height, atmospheric pressure and precipitation. This information is usually recorded by the ship's crew, and may be copied from the daily ship log.

Table 3.1 Data Collection Summary

Parameter	Sampling Instrument	Sampling Method	Analytical Instrument	Analytical Method	Reporting Units
Dissolved Oxygen	SeaBird (Model 11, 19 or 25) Winkler Titration	overboard deployment GLNPO QAPP 2001	Brinkman sensor NA	NA EPA #600/4-79-020	mg/L mg/L
Temperature	SeaBird (Model 11,19 or 25) Thermister thermometer	overboard deployment manual measurement of Niskin bottle	NA NA	NA NA	C C
Wind Direction	Wind Vane	compass scale	Ship instrument	NA	degrees
Wind Speed	Anemometer	gage	Ship instrument	NA	knots/hr
Wave Height	Watch Officer	observation	NA	NA	meters
Wave Direction	Watch Officer	observation	NA	NA	degrees
Barometric pressure	Barometer	observation	Ship instrument	NA	mm Hg
Secchi Depth	Secchi disk	overboard deployment (daylight)	NA	NA	meters
Total Phosphorous	Rosette sampler	overboard deployment	Lachat (at shore-based laboratory)	Lachat Manual	g/L

B2   Sampling Methods Requirements

B2.A. Equipment Required

SeaBird Data Logger. The SeaBird 9/11 (or SeaBird 19 or SeaBird 25) Data Logger instrument cluster contains modular sensors for depth, temperature and dissolved oxygen (as well as others), a submersible pump, a strain-gauge pressure sensor and a non-volatile CMOS semiconductor memory to provide a high-quality limnological profiling system. On the *R/V Lake Guardian*, the SeaBird 9/11 is attached to the Rosette sampler, and it is

connected to a computer system to permit real-time viewing of the profile data and to control the operation of the sampler.

The SeaBird 19 and SeaBird 25 instruments are used on alternate vessels when the *R/V Lake Guardian* is not available. They may also be used on the *R/V Lake Guardian* as backup units to the SeaBird 9/11. For use in Lake Erie, a stainless steel extension is attached to the housing to allow the instrument package to rest 0.5 meters off the bottom without pumping disturbed sediments across the sensors. A magnetic switch initiates recording, including a header record containing time, date and cast number. After a cast has been completed, the recorded data are downloaded to a computer for display, analysis and permanent archival. Alkaline batteries can be used to provide up to 24 hours continuous operation depending on configuration.

SeaBird software is regularly updated by the manufacturer. Reference manuals are available on the *R/V Lake Guardian* and should be consulted for troubleshooting or unfamiliar operation of the SeaBird. Current versions of the software are Microsoft Windows-based, and the on-screen prompts are clear.

IMB Compatible Computer. An Intel Pentium-compatible computer is required for running MS Windows operating system. SeaBird's SEASOFT software package provides real time data acquisition, as well as post-deployment retrieval, processing, display and archiving of data. The computer reduces raw data to engineering units (e.g., temperature voltage) and calculates derived variables (temperature, depth, dissolved oxygen concentration), and presents a video display in tabular or graphical form.

Rosette Sampler. The Rosette Sampler is used onboard the *R/V Lake Guardian* to collect water samples at designated depths for subsequent chemical and/or biological analysis. A 12-bottle Rosette sampler system (Sea-Bird Electronics 32 Carousel Water Sampler) will be used to collect water samples. This equipment allows an operator to remotely actuate a sequence of up to 12 water sampling bottles. This system consists of a CTD (conductivity, temperature and depth sensor - Sea-Bird Electronics Model 9 Underwater Unit) attached at the bottom of the Rosette, an A-frame, 1000 feet of multi-conductor cable, a variable speed winch and Sea-Bird Electronics Model 11 Deck Unit with attached computer. The CTD measures water depth and temperature, which is graphically (CRT) displayed onboard the research vessel. The bottles can be closed in any predetermined order, remotely from the deck of the vessel while the array is submerged at the various sampling depths. The Rosette sampler is equipped with 8-liter Niskin bottles.

Note: To maintain the DO probe in optimum condition: 1.) Use a 1% Triton X solution to wet the membrane between casts; and 2.) Keep a 5% solution of sodium sulfite in the probe between cruises. The Triton X keeps the membrane clean and the sodium sulfite retards the consumption of the probe internal material. Dispose of waste prior to using the Rosette according to the procedures in Section 7, of *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*, Attachment 3.

Dissolved Oxygen Sample Bottles and Laboratory Apparatus. Refer to the Attachment 3, *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*, for a list of sample bottles and necessary laboratory hardware and reagents.

B2.B. Data Acquisition - Operating the SeaBird and Rosette Sampler

<u>Deployment Strategy</u>. At each station visit, dissolved oxygen concentration, water temperature and depth will be recorded and stored by a SeaBird 9/11 (or SeaBird 19 or SeaBird 25) CTD Data Logger instrument package (or a later or other comparable instrument array) deployed from the *R/V Lake Guardian* or other suitable vessel. The SeaBird is attached to a steel cable and winch assembly which is used to control the rate of descent and retrieval of the instruments. The instrument is allowed to reach temperature equilibrium at a depth of 1 meter before being lowered through the water column at a rate approximately 0.5 meter/second. Readings from all sensors are automatically taken every 0.25 seconds. The instruments will be positioned within 1.0 meters off the bottom for at least 60 seconds to ensure all instruments have reached equilibrium with the temperature and dissolved oxygen concentration in the hypolimnion. Replicate casts will be made at every fifth (5th) station to confirm maintenance of precision characteristics of the instrument cluster. Ship crew (deck-hands and/or marine technicians) are generally available to assist the operation and deployment of sampling apparatus. It is the responsibility of the Project Leader, however, to ensure that all methods, procedures, and safety considerations are followed according to the QAPP.

<u>Deploying the SeaBird 9/11 and Rosette Sampler</u>. Ensure, via daily inspection, that the Rosette sampler, SeaBird instrument array, and all connections are well secured, and that there is no apparent excessive wear on critical parts. Before deploying the Rosette array, uncover the pH meter and remove the plastic Tygon tube at the inlet of the water supply to the SeaBird instrument cluster. Lower the Rosette array gently into the water to a depth of 1 to 2 meters to fully submerse it. Using the Seasoft software, turn on the pump, note the time and make weather observations. Wait another 2 minutes (3 minutes total) to allow the DO probe to equilibrate to the water temperature and ionic strength.

Make a slow downcast, about ¼ to ½ meter/second.

Monitor the array's sonar altimeter. If the bottom sensor is operational, the Rosette is lowered to 1 meter from the bottom. Allow the SeaBird to continue taking readings for 1 minute to ensure that the dissolved oxygen probe has reached equilibrium. If the bottom sensor is not operating, the Rosette is lowered so that it touches the bottom and is then raised at least 1 meter from the bottom. The operator will wait 3 minutes to allow the sampler to drift away from the disturbed area before the Rosette sampler will be lowered to B-1 and the sample taken.

Close (fire) two Niskin bottles to obtain duplicate water samples at the B-1 meter depth.

Raise the array <u>slowly</u> to get a good upcast for dissolved oxygen in the hypolimnion, at least through the thermocline. At one meter below the surface, stop the array for one minute to continue taking SeaBird readings. Fire two more Niskin bottles.

Return the Rosette to the deck rack, and terminate Seasoft logging of the cast. Inspect the Niskin bottles and the log to see that the profile obtained is adequate and the samples were successfully collected. Reattach the Tygon tubing to the water inlet for the DO sensor and fill it with D.I. water.

Take surface water temperature from the top of an appropriate Niskin bottle, and obtain water samples from Niskin bottles for determinations of Winkler method DO, and, as needed, for total phosphorous.

Processing the SeaBird Data. A graphic profile of temperature - depth and of dissolved oxygen - depth will be displayed, and if possible, printed immediately and inspected for any anomalies or obvious problems with the instrumentation.

The SeaBird data files must be further processed to retrieve the instrument readings for temperature and dissolved oxygen at designated depths. The program DATCNV.EXE (or its updated equivalent) converts raw data from the SeaBird files (.DAT or .HEX) to engineering units and stores the converted data in a file with extension .CNV. The .CNV file can be viewed with a Word Processor to retrieve the instrument readings for each scan.

The program BINAVG.EXE (or its updated equivalent) averages the data in converted data (.CNV) files. The averaging option should be set to 0.5 meter depth intervals. The output from this program can be written back to the .CNV file, and the results displayed with a Word Processor. For each of the designated depths, the corresponding temperature and dissolved oxygen concentration is recorded from the closest 0.5 meter interval average. Use underline downcast data for the epilimnion and the upcast for the hypolimnion values. Record the values on the data sheets.

B2.C. Deploying the SeaBird 19 or SeaBird 25, Independent of the Rosette Sampler

If the field operations are being conducted on a vessel other than the *R/V Lake Guardian*, or if the SeaBird 9/11 unit is unusable, the SeaBird 19 or SeaBird 25 units may be deployed to get water column profiles of depth, temperature and dissolved oxygen. On the *R/V Lake Guardian*, these units my still be connected to a computer to obtain real-time profiling information. On most other vessels, the units will be deployed without real-time capability, and the data will be downloaded to a computer at the end of each cast.

Note: Comparisons of SeaBird 9/11 and SeaBird 25 or SeaBird 19 should be run prior to SeaBird 25 or SeaBird 19 use on an alternate vessel. T-Test statistical comparison ($P \geq 0.05$) should be run for the integrated averages of hypolimnion and epilimnion temperatures and dissolved oxygen values, and hypolimnion thickness (See B10: Data Management: Calculation of Dissolved Oxygen Depletion Rate). If P-values are not statically acceptable alter the SeaBird 25 or SeaBird 19 calibration coefficients such that the temperature and dissolved oxygen profiles are consistent (avoiding the introduction of bias through the use of multiple instruments) and re-run T-test.

The computer software to communicate with and control the function of the SeaBird units is different for each model SeaBird. The software manual should be consulted prior to operating the SeaBird units to confirm that the appropriate software is being used. The following procedures provide general guidance on remote deployment of a SeaBird unit, but operating commands and other instructions and warnings are listed in the manuals.

Check that the computer cable is connected to SeaBird unit.

Run the communications program (e.g., Term19 or Term25 or their equivalent upgrade), and establish that the SeaBird has sufficient memory and battery power to complete the intended cast. Generally, this is not a problem and can be checked at the start of each sampling day.

Disconnect the computer cable from SeaBird, and install the electrical connector <u>plug</u> on SeaBird, for a water seal over the electrical terminals. Screw on the locking outer hard plastic cap to seat the inner rubber plug.

Remove the Tygon tubing from the water inlet to the conductivity and DO probes.

Place the SeaBird on the cage extension, matching the rectangular SeaBird cage with the extension top rectangle. Clamp the SeaBird and cage extension together.

Attach the SeaBird to the hydro wire with the "D" buckle from the cage to the wire loop, not the hook. Fasten the safety line from the SeaBird cage to the hydro wire, independently of the hooks, rings or clamps normally used to attach the SeaBird to the wire.

Switch **ON** the SeaBird just before deploying the instruments into the water. The switch is a rectangular 1 inch by 3 inches white plastic block that slides near the bottom of the instrument cluster.

Set the meter wheel of the deploying cable to "0" with the bottom of the SeaBird cage at the surface of the water. Then lower the SeaBird 1 meter to fully submerse it.

Wait at least 40 seconds for the DO water pump to come on. The pump activates 40 seconds after the conductivity probe registers a certain minimum conductance.

Wait another 2 minutes (3 minutes total) to allow the DO probe to equilibrate to the water temperature and ionic strength.

Make a slow downcast, about ¼ to ½ meter/second.

With the SeaBird at the bottom resting on the cage extension, allow the SeaBird to continue taking readings for 1 minute.

Raise the SeaBird <u>slowly</u> from the bottom to get a good upcast for dissolved oxygen in the hypolimnion, at least through the thermocline.

Retrieve the SeaBird onto deck. <u>Turn off the switch.</u> <u>Reattach the Tygon tubing to the water inlet for the DO sensor and fill it with D.I. water.</u> Position portable notebook computer (computer connector cable) within reach of SeaBird. If portable notebook computer is not available bring the SeaBird back into the lab.

Remove the electrical connector's water plug from the SeaBird. Attach the computer cable. On the plug and the cable receptacle is a raised dot that marks the location for a larger pin. The raised dot goes to the outside of the cage, parallel to the heavy cross brace

Re-establish communications with the SeaBird unit, and follow software instructions for downloading and saving the computer files of the cast just completed.

A graphic profile of temperature - depth and of dissolved oxygen - depth will be displayed immediately and inspected for any anomalies or obvious problems with the instrumentation. From the temperature-depth trace,

the depths are determined for the parts of the thermal structure. The computerized data are averaged in 0.5 meter intervals using software designed by the CTD manufacturer. For each of the designated depths, the corresponding dissolved oxygen concentration is recorded from the closest 0.5 meter interval average. **Follow the procedures in Section B2.B for "Processing the SeaBird Data."**

[Important tip: If a SeaBird 25 cast profile for dissolved oxygen appears erratic or perhaps unresponsive to water column conditions, even though the temperature profile appears proper, CHECK THE INSTRUMENT STATUS HEADERS FOR THE MINIMUM CONDUCTIVITY REQUIRED TO TURN ON THE PUMP. It should be "0." Higher numbers are used for seawater, and the pump will not operate in fresh water.]

B2.D Safety

During the deployment of sampling equipment, all established ship safety procedures for deck work will be observed, including the wearing of work vests, avoidance of swinging objects, caution on wet slippery decks, etc. In the laboratory, all requirements of the GLNPO laboratory safety manual will be followed for each procedure so referenced.

B3   Sample Handling and Custody Requirements

All field data forms and portable memory devices will be labeled at the time data are collected with the survey designation, station numbers, date, and sample numbers. The EPA Project Leader will maintain custodial responsibility for all electronic project data files and original hard-copy forms at the GLNPO office in Chicago. The EPA Project Leader or his designated representative shall maintain personal custody of the electronic files and hard-copy during the transfer from the research vessel to the Chicago office.

Samples for Winkler dissolved oxygen analysis are analyzed within 2 hours of collection, therefore, no holding time or chain of custody procedures need be established.

Bottles containing samples to be analyzed for total phosphorous will be clearly labeled with preprinted identification, including survey designation, station, depth strata, and sample number. Analysis request sheets will be completed for each survey, and they will serve as inventory of all collected samples. Chemical analyses of the samples may also be performed onboard the *R/V Lake Guardian*, although not necessarily concurrently with the Lake Erie Central Basin surveys for dissolved oxygen. If the samples will not be analyzed within 48 hours from the end of a survey, they will be stored onboard in the laboratory walk-in refrigerator, sealed in a clearly labeled box with a copy of the data analysis request sheets. If the samples are collected from another vessel, they will be sealed with a copy of the data analysis request sheets in a clearly labeled box, and transferred to the *R/V Lake Guardian* with another copy of the data analysis request sheets.

The shipper will sign the data analysis request sheet confirming that the contents of the box are reflected accurately on the sheet. The receiver in the laboratory will inventory the contents of the box and record any missing samples or sample problems (e.g., leaking bottles) on the sheets. The receiving person also will sign the form, and a copy will be sent to the Project Leader for records.

B4   Analytical Methods Requirements

Winkler Method for Dissolved Oxygen Concentrations

Analysis of water samples for dissolved oxygen concentrations by the Winkler method will follow the *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*, see Attachment 3.

Analysis of Water Samples for Total Phosphorous

The method for analysis of total phosphorous in water samples will be identical to those presented in *Quality Assurance Project Plan, Great Lakes Survey Studies of Lakes Michigan, Huron, Erie, Ontario and Superior*.

Interferences

No interferences are anticipated to the chemical analyses or SeaBird sensors. Caution must be maintained, however, to avoid excessively disturbing the bottom sediments before sampling. Sediment resuspension can affect total phosphorous concentrations and may result in samples being unrepresentative of the bottom waters. Evidence of sediment disturbance will be found in obviously turbid water samples from the bottom sample Niskin bottle.

B5   Quality Control Requirements

See Section A7, Quality Objectives & Criteria for Measurement Data.

Quality control will be maintained by comparison of data from replicate samples obtained electronically, from replicate dissolved oxygen titration samples, and between electronic and titration results. Preliminary data comparisons will be made at the time of sampling at each station to ascertain if there is any indication of equipment or procedural error. Differences in surface temperatures of more than 1°C as measured by a thermometer and compared with probe readings will be treated as suspect readings and temperature profiles rerun if necessary. Differences in dissolved oxygen readings of more than 1 mg O_2/liter as measured by Winkler method and compared with probe readings will be treated as suspect and additional dissolved oxygen measurements will be made.

Corrective Actions

Any corrective actions in the field that may be needed to ensure complete and accurate data collection will be the responsibility of the EPA Project Leader or his/her representative.

The following actions may be implemented to correct apparent erroneous data:

1.   RPD for dissolved oxygen exceeds limits of acceptable accuracy

   A.   Re-sample for Winkler titration.
   B.   Recast the SeaBird instrument package, ensuring adequate time for equilibration of the oxygen probe at the depth in question.

C.   Check calibration coefficients of SeaBird dissolved oxygen sensor by manufacturers methodology. Re-test RPD with new coefficients applied to raw SeaBird data.

D.   If a <u>SeaBird 25</u> cast profile for dissolved oxygen appears erratic or perhaps unresponsive to water column conditions, even though the temperature profile appears proper, CHECK THE INSTRUMENT STATUS HEADERS FOR THE MINIMUM CONDUCTIVITY REQUIRED TO TURN ON THE PUMP. It should be "0." Higher numbers are used for seawater, and the pump will not operate in fresh water.

E.   Recast with alternate SeaBird instrument package.

2.   Probe readings for dissolved oxygen consistent with nearby stations and expectations, but not in agreement with Winkler

A.   Re-sample for Winkler titration.

B.   Confirm reagent integrity with titration of a 100% saturation sample.

3.   Winkler dissolved oxygen replicates consistent, but not in agreement with probe values.

A.   Re-sample for Winkler titrations, being careful to deploy the Niskin bottle at the correct depth.

B.   Recast the SeaBird, ensuring adequate time to equilibration of the instrument sensors at the depth in question.

4.   Replicate readings for a given sampling method are inconsistent

A.   Repeat sampling and run additional replicate analyses until consistency is achieved, or the cause of inconsistency is found and corrected.

5.   Temperature RPD exceeds limits of acceptable accuracy

A.   Re-sample thermometer reading, being sure to avoid influences of rapid heating or cooling of the sample due to air temperature.

B.   Recast the SeaBird instrument, allowing adequate equilibration of the temperature sensor at the same depth as the Niskin bottle deployment.

A complete data check within and between sampling station data sets will be conducted after each sampling cruise when data have been returned from the laboratory. The criteria for acceptable data, previously identified in Section A7, will be followed. In addition, quality control charts plotting temperature and dissolved oxygen RPDs on a station-by-station basis will be used to identify any data errors and determine any trends or bias that may be developing.

B6   Instrument/Equipment Testing Inspection and Maintenance Requirements

All sampling equipment and instruments will be checked after completion of each sampling survey to determine condition. Broken or worn equipment will be repaired or replaced prior to initiating the next survey. Ship sampling gear (Niskin bottles, Rosette sampler, winches, etc.) are maintained routinely by the contracted ship

operators. The SeaBird instrument packages are checked, serviced and re-calibrated at the factory before the start of the sampling season, and as required during the year.

Daily SeaBird care includes keeping the dissolved oxygen sensor wet with distilled or deionized water when not immersed in lake water. A Tygon tube filled with D.I. is kept on the inlet to the oxygen sensor.
Periodic SeaBird care, at the end of intensive sampling days and at the end of each sampling survey, includes rinsing the oxygen sensor with 10% solution of Triton - X (surfactant recommended by the manufacturer) followed by warm water from tap, followed by a rinse with deionized water.

In addition, to maintain the DO probe in optimum condition: 1.) use a 1% Triton X solution to wet the membrane between casts; and 2.) keep a 5% solution of sodium sulfite in the probe between cruises. The Triton X keeps the membrane clean and the sodium sulfite retards the consumption of the probe internal material. Dispose of waste prior to using the Rosette according to the procedures in Section 7, of *Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration*, Attachment 3 of this document.

B7   Instrument Calibration and Frequency

SeaBird instrumentation

The manufacturers' specifications for the SeaBird CTD data logger instrument package include the following:

Parameter	Range	Accuracy	Resolution
Depth	0 to 600 m	+/- 0.02%	0.001%
Temperature	-5 to 35 C	+/- 0.004 C	0.0003 C
Dissolved Oxygen	0 to 15 mg/L	+/- 0.14 mg/L	0.007 mg/L

The SeaBird sensors are factory calibrated, and generally do not require regular adjustment. If independent measurements of the same water indicate that one or more sensors are providing inaccurate measurements, calibration procedures are provided by the manufacturer. Most calibrations involve measurement of voltage potentials under defined conditions, and subsequent adjustments to calibration coefficients embedded in the software controls. The user's manual should be consulted for calibration procedures and coefficient values for each specific sensor, should adjustments be required. In the event a newer or different model of SeaBird or another make of sensor array is utilized, comparable and appropriate procedures will be employed.

Confirmation of faulty calibration by independent measurements (thermometer measurements of surface temperature, Winkler dissolved oxygen titrations, or independent calibrated depth sensor) do not negate SeaBird data; correction factors can be calculated and new calibration constants entered into the software. Each station data may be re-analyzed with new calibration constants at a later date, if appropriate. The dissolved oxygen sensor is the one most subject to calibration error. Procedures are provided for measuring 100% and 0% saturation levels, and for assessing calibration constants, although these are not easily performed in the field onboard the research vessel. These checks will be attempted if the Winkler dissolved oxygen titrations confirm that present software settings are in error.

Winkler Titrations for Dissolved Oxygen

Winkler titration chemicals will be prepared by contract laboratory chemists prior to the dissolved oxygen surveys, and their concentrations confirmed by standard techniques. Titrations of water samples with 100% oxygen saturation will be conducted at the start of each survey day to confirm reagent integrity and strength.

B8   Inspection/Acceptance Requirements for Supplies and Consumables

The Project Leader is responsible for ensuring that all supplies and consumables are available and of good quality. Supplies consumable supplies may include chemical reagents for Winkler titrations, plastic bottles and caps for water samples for total phosphorous analysis, and laboratory supplies such as disposable gloves and toweling.

B9   Data Acquisition Requirements (Non-direct Measurements)

No non-direct measurements are required for this project. Comparison of data from this project with historic data will rely on the integrity of published data in peer-reviewed literature and/or government reports.

B10   Data Management

Data Recording

Field data will be recorded on standard field data forms (See Attachment 2, *Dissolved Oxygen Survey – Lake Erie Central Basin Dissolved Oxygen Data (Winkler)*). SeaBird data files will be copied to hard disk and to CD or DVD or memory stick as backup. Graphic plots of depth versus dissolved oxygen and of depth versus temperature from the SeaBird data will be printed for each station visit. A tabular computer printout of the SeaBird data averaged in 0.5 meter intervals at each station will made, and it shall include depth, dissolved oxygen and temperature data.

All hard-copy of data and summarized information for each station will be stored in the field in a 3-ring binder for safekeeping and reference.

Storing and Backing Up Computer Files

At the conclusion of each survey, all original field data sheets will be compiled into one loose leaf notebook and retained in the Offices at GLNPO.

A photocopy will be made of each original sheet, and compiled into a second notebook for transport to the field on subsequent surveys.

All SeaBird electronic files will be backed up to 1) CD, DVD and/or memory stick, and 2) subdirectory on hard disk. All portable memory devices will be stored in the Offices at GLNPO.

All data on the field data sheets will be transferred to an electronic spreadsheet for data reduction and summarization. The spreadsheet will be maintained and backed up by the Project Leader.

Dissolved Oxygen Concentration Data

SeaBird electronic data files, graphic plots and tabular printouts will be retained for reference and analysis. Data from the designated depths for each station each survey will be entered into a spreadsheet for further analysis and summary statistics. Scientific graphing software will be used to generate plots of dissolved oxygen concentrations throughout the stratified season.

Calculation of Dissolved Oxygen Depletion Rate

The rate of dissolved oxygen depletion will be calculated, adjusted for vertical mixing and seasonable variability, and normalized to constant temperature and hypolimnion thickness according to procedures recommended by F. Rosa and N.M. Burns. 1987. *Lake Erie Central Basin Depletion Changes from 1929-1980*, **J. Great Lakes Res**. 13(4):684-696. The DOS-based computer program **OXRATES**, written for GLNPO by C. O'Leary (1990) has been used to perform this calculation. However, beginning in 2005, **LakeErieDOv4.0** (Microsoft Access), written for GLNPO by Computer Sciences Corp, Alexandria, VA was introduced. Annual comparison between these programs will continue through the 2007 sampling season, at which point **LakeErieDOv4.0** (Microsoft Access) will be used exclusively.

1. Calculate the average values of epilimnion temperature, hypolimnion temperature, epilimnion dissolved oxygen, hypolimnion dissolved oxygen, hypolimnion thickness, and Julian day for the interval for each station.

    i.e., $O_e = (O_{e1} + O_{e2}) / 2$

2. Calculate the uncorrected oxygen depletion rate, R_o, for the first station based on this equation:

    $R_o = ((O_{h1} - O_{h2}) / (Julian_2 - Julian_1)) * 30$

3. Calculate the oxygen depletion rate adjusted for vertical mixing, R_v, for the first station based on this equation:

    $R_v = [((O_e - O_h) / (T_e - T_h)) * (T_{h2} - T_{h1})] + R_o$

    Averages for the interval for O_e, O_h, T_e and T_h are used.

4. Calculate the oxygen depletion rate adjusted for temperature, R_q, for the first station based on these equations:

alpha	=	$10 / (T_h - 10)$ or $10 / (10 - T_h)$
R_q	=	10 to the power of $[\log R_v - (\log 2 / alpha)]$ for $T_h > 10$
R_q	=	10 to the power of $[\log R_v + (\log 2 / alpha)]$ for $T_h < 10$

    Average for the interval for T_h is used.

5. Calculate the oxygen depletion rate adjusted for hypolimnion thickness, R_t, for the first station based on these equations:

KS	=	5.89
KW	=	1.90

$$\text{thick} = \text{(bottom depth - top of the hypolimnion depth)}$$
$$q_t = R_q - ((\text{year} - 1928) * 0.028)$$
$$f_t = q_t / ((KS / \text{thick}) + KW)$$
$$SOD = (f_t * KS) / 4.7$$
$$R_t = SOD + f_t * KW + (R_q - q_t)$$

Average for the interval for thick was used.

6.   Calculate the oxygen depletion rate adjusted for seasonal effects, R_c, for the first station based on this equation:

$$R_c = R_t + ((\text{Julian} - 75) * 0.012) \quad \{\text{May } 1 = 1\}$$

Average for the interval for Julian was used.

7.   Repeat steps 1 through 6 for the rest of the stations.

8.   Calculate the mean and standard error for R_o, R_v, R_q, R_t, and R_c for the interval.

*   Note that the means are calculated after all of the adjustments are made. The mean value is never used in calculations.

**   The notations used in the equations are based on those used in Rosa and Burns (1987).

For **OXRATE**, an input ASCII data file is required. Each of ten (10) columns of data represent data from the same station for all station visits. The columns are *space* delimited. The rows represent the following format:

1.   File Header "Temperature and Dissolved Oxygen for Lake Erie 1992"
2.   Number of Surveys   Number of Stations   (5 10)
3.   Year   Dates of First Survey   (1992   June 2-4)
4.   Temperature at Surface
5.   DO concentration at Surface
6.   Temperature at Mid-epilimnion
7.   DO concentration at Mid-epilimnion
8.   Temperature at 1 meter above thermocline
9.   DO concentration at 1 meter above thermocline
10.   Temperature at mid-thermocline
11.   DO concentration at mid-thermocline
12.   Temperature at 1 meter below thermocline
13.   DO concentration at 1 meter below thermocline
14.   Temperature at mid-hypolimnion
15.   DO concentration at mid-hypolimnion
16.   Temperature at 1 meter above bottom
17.   DO concentration at 1 meter above bottom
18.   Date the station was sampled
19.   Bottom depth
20.   Top of hypolimnion depth
21.   Julian day station sampled

22. Year   Dates of 2nd survey (1992   June 23-25)
23. Temperature at Surface
.. etc.

Missing data are represented by -999. If data from only one or two depths are available within epilimnion or hypolimnion, the data are considered representative of that water layer, and the table is completed with averages for that station and water layer.

For **LakeErieDOv4.0**, input all data files (.HEX or .DAT) into database, adjusting final upper-hypolimnion if needed. Run "Calculate Oxygen Depletion Rate" function, which integrates the continuous data profile producing a two (2) layer (epilimnion and hypolimnion) temperature and dissolved oxygen model. See software manual for additional instructions (see Attachment 4, *Lake Erie Dissolved Oxygen Depletion Tool User's Guide*).

Assessment/Oversight

C1   Assessment and Response Actions

Performance and System Audits

The EPA Project Leader will maintain records of project performance, including data collection, SeaBird operation, QC protocols, data validation and data reduction. A review of procedures will be conducted with field personnel before each survey, and a review of survey operations will be conducted at the conclusion of each survey. Any persistent problems that jeopardize the program will be brought to the attention of the Chief, Monitoring, Information and Reporting Branch at GLNPO for resolution.

Procedures to be used to Assess Data Precision, Accuracy and Completeness

The sampling methodology, utilizing both electronically-recorded and manual methods of measuring dissolved oxygen, temperature and depth at each station, along with replicate sampling used for both methods, provides on-site data comparisons that would indicate any errors. Replicate samples for each sampling method provide a method for assessing data precision. Relative comparisons of data gained from Winkler versus probe data for dissolved oxygen and thermometer versus probe data for temperature will be used to assess data accuracy. Completeness of sampling data at each station is ascertained from manually logging temperature, dissolved oxygen and sampling depth for each strata sampled, noting depths not sampled, and by computerizing and storing electronically recorded temperature and dissolved oxygen profiles on computer hard disk and portable memory devices. Any sampling bias will be detected by control charts for individual station data sets.

Decision for Corrective Action

Quality control checks are incorporated into each station visit. The Project Leader, or the designated shift leader, will assess the QA/QC measurements for dissolved oxygen and temperature and determine if corrective action is needed. See Section B5 for possible actions to confirm and/or correct perceived problems with either Winkler titrations or SeaBird probe readings. In most cases, the SeaBird sensors will NOT be re-calibrated during the course of survey. Consistency of probe readings should be maintained, if possible. Adjustments to

SeaBird instrument bias can be made post-cruise via software coefficients. However, the cause for concern and magnitude of the problem should, in all cases, be recorded and reported to the Project Leader for resolution.

C2 Reports to Management

Reporting

Summary reports of the dissolved oxygen concentrations and depletion rates at the end of the field season will be prepared by the Project Leader. Recipients of the report will include GLNPO management, GLNPO Report to Congress, EPA ORD, Environment Canada and the International Joint Commission.

Quality Assurance Reports

Quality assurance reports will be prepared at the conclusion of the sampling season and submitted with the data analysis report to the Chief, Monitoring, Information and Reporting Branch at GLNPO. These reports will contain an evaluation of results from performance and system audits, an assessment of data accuracy and completeness, and the definition of any persistent project problems with recommended solutions. Quality assurance summaries will also be included as part of technical data and interpretive reports that may be distributed to Great Lakes scientists or to the public.

Data Validation and Usability

D1 Data Review, Validation and Verification Requirements

Data Validation

The criteria for acceptable measurements of dissolved oxygen and temperature are defined in Section A7, Quality Assurance Objectives for the project. Data will be considered acceptable if the Objectives for each station have been met. Scrutiny of thermal and dissolved oxygen profiles from each station will confirm data integrity. Data from any station visit in which the Objectives were not met and not corrected on site will be subject to intense review, including comparison with data from neighboring stations and historic data, to determine the likely cause of the discrepancy, and to adjust SeaBird values if appropriate based on computation constants. Suspect data for which no justification for adjustments can be found will be rejected.

Data validation for total phosphorous will follow all procedures as defined in *Quality Assurance Project Plan, Great Lakes Survey Studies of Lakes Michigan, Huron, Erie, Ontario and Superior*.

D2 Validation and Verification Methods

Process for data validation and verification

The Project Leader, or a technical representative, will conduct a 100% audit of all data collected and entered into electronic format. The audit will include the following assessments:
1) That the data have met quality assurance objectives for the project.
2) That the calculations have been conducted properly.

3) That any data reduction and summary information are proper and consistent with project objectives.
4) That data have been transcribed from the field data sheets to electronic format accurately.

Should discrepancies be found, the Project Leader will consult with the associates involved in the field work or data analysis and attempt to find the cause and nature of the problem. The Project Leader will have final responsibility for approving the use and/or release of the project data.

Conveying results of data verification and validation

The Project Leader will provide a statement of data quality, including any caveats or explanatory remarks, to accompany the data to outside users. Such a statement will be included in the permanent electronic archive for the data in the GLNPO database, and it will also accompany the data when posted on the GLNPO web page.

D3   Reconciliation with Data Quality Objectives

The Project Leader will determine if the data do not meet the stated Data Quality Objectives, and if additional reconciliation is needed. If consistent, serious problems persist, the Project Leader will consult with the GLNPO Quality Assurance Team and with the Chief, Monitoring, Indicators and Reporting Branch, to determine if the entire project data set should be rejected, or if parts of the data remain useful. For example, circumstances may prevent obtaining sufficient data for the calculation of dissolved oxygen depletion rate for the season, but users would still wish to know the areal extent and severity of the maximum oxygen depletion at the end of the season.

ATTACHMENT 1 – DISSOLVED OXYGEN SURVEY STATIONS – LAKE ERIE CENTRAL BASIN

Dissolved Oxygen Survey Stations
Lake Erie Central Basin

30

38   31

37   32
73   78

36

43
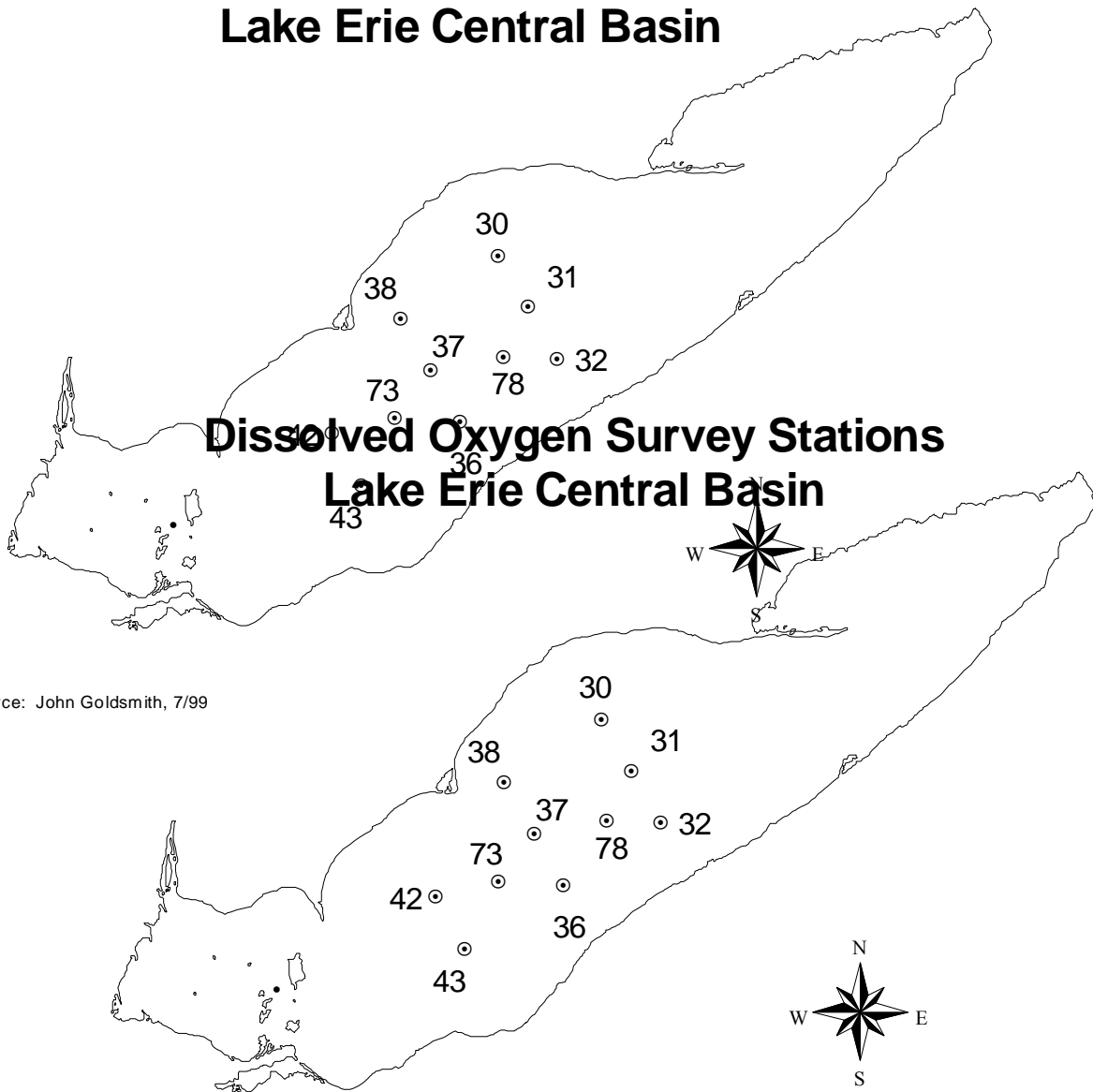
Source: John Goldsmith, 7/99

30

38   31

37   32
73   78

42

36

43

ATTACHMENT 2 – DISSOLVED OXYGEN SURVEY – LAKE ERIE CENTRAL BASIN DISSOLVED OXYGEN DATA (WINKLER)

Dissolved Oxygen Survey - Lake Erie Central Basin Dissolved Oxygen Data (Winkler)

Survey ID	Visit ID	Station ID	Analytical Batch ID	Analytical Date (mm/dd/yyyy)	Analytical Time (Shiptime, military)	Analyst (initials)XXX

Sample ID	Titrant Used D.O. (mL)	BOD Bottle Volume (mL)	Vol. Corrected D.O. (mg/L)	Temp. (Celsius)	Barometric Pressure *(mb)	Corrected Table Value (mg/L)	Remarks
0							
0							
0							
0							
0							
0							
0							
0							

Calculation of Vol. Correct D.O.

Titrant Used (ml) x 60.8 (ml) / BOD Bottle Volume (ml)

Saturation Value determined by multiplying TableValue(Temperature table) by actual barometric pressure over standard barometric pressure

Corrected Table Value

Value from temperature table x barometric pressure/std. pressure

At least one saturated sample is analyzed on each shift

Method Performance Criteria		
QC Type	**Minimum Performance**	**Acceptance Criteria**
Lab Duplicate	Non-DO Surveys: Run on one depth from approximately three predesignated stations per lake	Absolute Difference <0.2 mg/L
	DO Surveys: All SRF and B- samples at each station	

| Lab Accuracy Check, Saturated Sample | Non-DO Surveys: Coinciding with the first running of Winkler QC checks in each lake | ± 0.5 mg/L, compared to theoretical |
| | DO Surveys: At the beginning and once per shift | |

**ATTACHMENT 3 – STANDARD OPERATING PROCEDURE FOR DISSOLVED OXYGEN MICRO
METHOD, WINKLER TITRATION**

Standard Operating Procedure for Dissolved Oxygen Micro Method, Winkler Titration

1.0   Scope and Application

1.1   This method is applicable to surface waters and other "clean" water.

1.2   The probe method may be used under any circumstances as a substitute for the modified Winkler procedure, provided that the probe itself is standardized against the Winkler method on samples free of interfering materials.

1.3   The sensitivity of the method is approximately 0.1 mg/L.

2.0   Summary of Method

2.1   The sample is treated with manganous sulfate, potassium hydroxide, and potassium iodide (the latter two reagents combined in one solution) and finally sulfuric acid. The initial precipitate of manganous hydroxide, $Mn(OH)_2$ combines with the dissolved oxygen (DO) in the sample to form a brown precipitate, manganic hydroxide, $MnO(OH)_2$. Upon acidification, the manganic hydroxide forms manganic sulfate which acts as an oxidizing agent to release free iodine from the potassium iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate

2.2   The reagents are prepared prior to the cruise at the support laboratory.

2.3   During the first day of the cruise prior to sampling, the 0.0075 N thiosulfate is prepared and standardized according to Sections 6.7 and 6.12. Reagents #1 and #2 are checked according to Sections 6.2 and 6.3 to determine their background oxidation capability. If there is a color, titrate with the 0.0075 titrant until clear and record one half the volume as $MnSO_4$ blank and/or alkaline iodide blank. To verify that the procedure is operational, a high control check or spike is run in duplicate. The results should agree within 0.2 mg/L and should agree with the calculated value within 0.5 mg/L.

3.0   Sample Handling and Preservation

3.1   Samples are collected and transferred to 60-mL glass BOD bottles. Special precautions are required to avoid entrainment or solution of atmospheric oxygen or loss of dissolved oxygen.

3.2   DO must be determined immediately at the collection site. There is no holding time.

4.0   Interferences

4.1   There are numerous interferences to the dissolved oxygen test, including oxidizing and reducing agents. For clean samples, such as lake water, chemical interferences are minimal and ignored.

5.0   Apparatus

5.1   Incubation bottles, 60-mL, such as Wheaton Scientific #227494

5.2   Burets, 25-mL, accurate to 0.05 mL

5.3   Volumetric flask, 1-L

5.4   Graduated cylinders, 500-mL and 100-mL

5.5   Pipettors, 0.4-mL, such as Eppendorf

5.6   Propipetors with plastic parts for Reagents #1 and #2, 0.4-mL delivery volume

6.0   Reagents

6.1   Reagent water: Throughout this SOP "water" is understood to mean reagent water, unless otherwise
        specified, and "dilute," used as a verb, means dilute with reagent water.

6.2   Manganese sulfate solution: Dissolve 120 g $MnSO_4 4H_2O$, 100 g $MnSO_4 2H_2O$, or 91 g $MnSO_4 H_2O$ in
        water and dilute to 250 mL in a graduated cylinder or bottle marked at 250 mL. Test this solution by
        adding 0.8 mL to a solution containing 100 mL of water, 10 mL 10% sulfuric acid, 10 mL 10% KI and
        starch indicator. There should be no color.

6.3   Alkaline iodide reagent: Dissolve 125 g NaOH (or 175 g KOH) and 33.8 g NaI (or 37.5 g KI) in water
        and dilute to 250 mL in a cylinder or bottle marked at 250 mL. Test this solution by adding 0.8 mL to a
        solution containing 100 mL of water, 10 mL 10% sulfuric acid and starch indicator. There should be no
        color.

6.4   Sulfuric acid, concentrated.

6.5   Starch indicator solution: Dissolve 2 g laboratory grade soluble starch and 0.2 g salicylic acid, as a
        preservative, in 100 mL hot water.

6.6   Sodium thiosulfate stock solution, 0.0375 N: Dissolve 9.3075 g $Na_2S_2O_3 5H_2O$ in water and add 0.6 g
        NaOH or 15 mmol and dilute to one liter.

6.7   Sodium thiosulfate standard titrant, 0.0075 N: Dilute 200 mL (or an appropriate volume) of stock
        solution (6.6) to 1 liter. Standardize according to Section 6.12. Prepare weekly.

6.8   Potassium biiodate stock solution, 0.15 N: Dissolve 4.873 g of $KH(IO_3)_2$ (previously dried at 103 C
        for two hours) in water and dilute to 1 liter.

6.9   Potassium biiodate working standard, 0.0375 N: Dilute 250 mL of stock solution (6.8) to 1 liter.

6.10   Potassium iodide solution, 10%: Dissolve 10 g of KI in water and dilute to 100 mL.

6.11   Sulfuric acid, 10%: Carefully add 50 mL of concentrated sulfuric acid to 460 mL of water.

6.12   Standardization of 0.0075 N sodium thiosulfate: Add 10 mL of 10% KI (6.10) and 10 mL of 10% H_2SO_4 (6.11) to 100 mL of water, followed by 4 mL of potassium biiodate working standard (6.9). Place in the dark for 5 minutes and then titrate with sodium thiosulfate standard titrant (6.7) to a pale straw color. Add 1-2 mL of starch solution (6.5) and continue the titration dropwise until the blue color disappears. Run in duplicate. Titrant necessary should be 20 mL.

    6.12.1 If the titrant (sodium thiosulfate) volume is greater than 20 mL, it is too weak. The following equation is used to calculate the volume of 0.0375 N sodium thiosulfate needed to adjust and increase the concentration of the titrant to 0.0075 N: (titrant-20) x 200/20. The calculated value derived from this equation is the volume of stock sodium thiosulfate that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate).

    6.12.2 If the titrant (sodium thiosulfate) volume is less than 20 mL, it is too strong. The following equation is used to calculate the volume of water needed to adjust and decrease the concentration of the titrant to 0.0072 N: (20-titrant) x 1000/20. The calculated value derived from this equation is the volume of water that needs to be added to, and per, one liter of titrant (0.0075 N sodium thiosulfate).

    6.12.3 After adjusting the concentration of the titrant, standardize the solution again. Repeat procedures outlined in Section 6.12, if necessary.

7.0   Procedure

7.1   The sample is transferred from the Niskin bottle by inserting the Niskin drain tube to the bottom of a 60-mL BOD bottle and allowing the sample water to overflow long enough to displace at least three volumes (180 mL).

7.2   Within ten minutes, using the propipetors, add 0.4 mL of the manganous sulfate solution, followed by 0.4 mL of the alkaline iodide solution (6.3) allowing the solutions to run down the neck of the bottle. Stopper the bottle, being careful to exclude any air bubbles, and mix well by repeated inversion of the bottle. When the precipitate settles to clear the upper a of the bottle, mix again by repeated inversion. After a second settling period produces an upper a of the bottle free of floc, remove the stopper and add 0.4 mL of concentrated sulfuric acid by allowing the acid to run down the neck of the bottle. Restopper, again being careful to exclude air bubbles, and mix by repeated inversion. Complete the analysis within 45 minutes of the acid addition.

7.3   Transfer the bottle contents to a 150- or 200-mL beaker and titrate with 0.0075 N thiosulfate solution (6.7) to a pale straw color. Add 1 to 2 mL of starch indicator and continue the titration to the first disappearance of the blue color. Record the mL of titrant and the volume of the BOD bottle.

7.4   Occasionally, a dark brown or black precipitate persists in the bottle after acidification. This precipitate will dissolve if the solution is kept for a few minutes longer than usual or, if particularly persistent, a few more drops of H_2SO_4 will effect dissolution.

8.0   Calibrations

8.1   Dissolved oxygen in mg/L is read directly from the buret if the BOD bottle is 60.8 mL, or else the value is the buret reading times 60.8 divided by the BOD bottle volume. Record the volume of titrant and the BOD bottle volume.

8.2   Calculation of DO from temperature and barometric pressure.

8.2.1   Prepare a saturated (with oxygen) water sample by vigorously shaking (10 - 15 times) a rigid plastic 960-mL bottle half full of reagent water or sample water. Obtain a barometer reading and measure the temperature of the saturated water. The following table can be used to obtain the mg/L DO at 760 mm Hg. Most barometers are corrected to sea level from their present elevation. This means that the true barometric pressure is equal to the barometric reading minus 18 mm (0.71 in) for Lakes Michigan, Erie, and Huron. The barometer reading in inches of mercury can be converted to millimeters by multiplying by 25.4, from millibars to millimeters of mercury, multiply by 0.75006.

8.2.2   Extrapolate DO solubility between whole temperature units for temperatures to 0.1°C. A table displaying extrapolated oxygen solubility in water to 0.1°C is located in **Attachment A** (*Extrapolated Oxygen Solubility in Water, Increments of 1 and 0.1 Degree Celsius)* of this standard operating procedure.

8.2.3   Adjust the extrapolated DO solubility for barometric pressure by direct ratio, i.e.,

$$\frac{\{Extrapolated~solubility~times~(corrected~barometric~pressure~-~18~mm)\}}{\{760~mm\}}$$

The true or actual barometric pressure is reportedly available on the Lake Guardian from the NEMA stream. The corrected to sea level values for Lake Michigan are also available from the barometer on the flying bridge. The current sea level pressure can also be obtained off the internet from the www.nws.noaa.gov current weather conditions aviation at the local airports.

Oxygen Solubility
Salinity less than 0.1 g/L, 760 mm Hg barometric pressure

Temp	DO	Temp	DO	Temp	DO	Temp	DO	Temp	DO
0	14.62	6	12.45	12	10.78	18	9.47	24	8.42
1	14.22	7	12.14	13	10.54	19	9.28	25	8.26
2	13.83	8	11.84	14	10.31	20	9.09	26	8.11
3	13.46	9	11.56	15	10.08	21	8.91	27	7.97
4	13.11	10	11.29	16	9.87	22	8.74	28	7.83
5	12.77	11	11.03	17	9.66	23	8.58	29	7.69

9.0 Quality Control

9.1 Two aliquots for duplicate analysis are taken directly from the Niskin bottle. On regular surveys, duplicate analyses are run on one depth from approximately three predesignated stations per lake. On DO surveys, duplicate analyses are performed on the surface and the B- depth samples at each Lake Erie Central Basin station.

9.2 Saturated sample analyses coincides with the first running of Winkler QC checks in each lake of a regular survey. At the beginning of each DO survey and daily thereafter, a saturated lake water sample is used to check for interferences or method error as described in Section 8.2. If the calculated value and the average determined value differ by more than 0.5 mg/L, the same test should be performed on reagent water. If a similar deviation is obtained on reagent water, then it can be assumed that method error is the problem, and corrective action should be initiated such as: re-standardize the titrant, check that the procedure is being performed correctly, etc.

9.3   The following QC samples must be prepared and analyzed at the minimum frequency indicated.

QC Type	Frequency	Acceptance Criteria
Lab Duplicate (LD1)	Non-DO Surveys: Run on one depth from approximately three predesignated stations per lake	Absolute Difference < 0.2 mg/L
	DO Surveys: All SRF and B-samples at each station	
Lab Accuracy Check, Saturated Sample (Sections 9.2 and 10.2)	Non-DO Surveys: Coinciding with the first running of Winkler QC checks in each lake of a regular survey	± 0.5 mg/L, compared to theoretical
	DO Surveys: At the beginning and once per shift	

9.4   Assessment

9.4.1   The analyst must compare analytical results to the acceptance criteria listed in Section 9.3 to identify QC failures. If the results are outside the acceptance criteria, the analyst should first review their calculations for errors and if none are identified, they must follow the corrective action procedures listed in Section 9.5.

9.5   Corrective Actions

9.5.1   Corrective action procedures will often be handled at the bench level by the analyst, who reviews the procedure for possible errors, checks calculations and any other potential sources of error. If the problem persists or cannot be identified, the matter must be referred to the Chief Scientist for further investigation. Depending upon the Chief Scientist's evaluation, the analyst may or may not be required to prepare and re-run the samples again. Once a decision is made, full documentation of the corrective action procedures and assessment of the final result must be filed with the WQS QM Technical Lead (Marvin Palmer) or the GLNPO QM.

9.6   Data Reporting/Recording
9.6.1   The analyst is responsible for identifying all failed QC samples in the remarks column of the Laboratory reporting forms. If analyses are being conducted onboard, the analyst should document the QC information on the hard-copy Field Information Recording Forms (Appendix H).

10.0   Summary

10.1   Thiosulfate standardization - at the beginning of each survey.

10.2   Saturated water samples are analyzed in duplicate and compared with the theoretical value (9.2 and 7) - at the beginning and once per shift on DO surveys and coinciding with the first running of Winkler QC checks in each lake for non-DO surveys.

10.3   Laboratory duplicate samples are analyzed - all surface and B- samples for DO surveys and on one depth from approximately three predesignated stations per lake for non-DO surveys.

11.0   Safety and Waste Handling

11.1   Refer to GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) and individual instrument procedural operations manuals for specific details on applicable 1) personal health and safety issues; 2) instrumental, chemical, and waste handling procedures; and 3) accident prevention. This applies to all EPA personnel, EPA contractors or federal, state, or local government agencies, and persons who operate or are passengers onboard US EPA GLNPO vessels during all activities and surveys.

11.2   All containers storing reagents, standards, controls, blanks, and wastes used in the laboratory must be properly identified through appropriate labeling and hazard definition.

11.3   Every chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Please refer to Appendix L in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended) for more detailed descriptions of the potential risks associated with any chemicals used in this method. It is good laboratory practice to wear a lab coat, safety goggles and gloves at all times.

11.4   It is the responsibility of the user of this method to comply with relevant chemical disposal and waste regulations as sited in GLNPO's *Health, Safety and Environmental Compliance Manual* (May 1997, or as amended). All applicable safety and waste handling rules are to be followed. Good technique includes minimizing contaminated waste.

11.5   Over-board discharges of chemical wastes are forbidden.

12.0   References

12.1   "Methods for Chemical Analysis of Water and Wastes," USEPA Publication #600/4-79-020, March, 1979.

12.2   "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 18th Edition, 1992.

**ATTACHMENT 4 – GLNPO'S OPEN LAKE SURVEY OF THE GREAT LAKES LAKE ERIE
DISSOLVED OXYGEN DEPLETION TOOL USER'S GUIDE**

1.0   Introduction

LAKE ERIE OXYGEN DEPLETION RATE CALCULATION TOOL

The Lake Erie Oxygen Depletion Rate Calculation Tool was designed to support the Great Lake National Program Office's (GLNPO's) Open Lake Survey of the Great Lakes, specifically the Dissolved Oxygen Survey of the Central Basin of Lake Erie. The tool functions to import physical and chemical data generated by an electronic CTD (conductivity, temperature, depth) computerized data recording module (such as the SeaBird Electronic, Inc. or modules used by Environment Canada). Dissolved oxygen (DO) concentrations are measured and recorded by a sensor integrated with the CTD instrument package. These data are exported into data files of a specific structure that are directly imported into the tool. The tool functions to calculate oxygen depletion rates for Lake Erie in milligram per liter per month for evaluation of ecosystem health and trend investigations. The procedure is as follows:

➢   import SeaBird or Environment Canada data files from the entire DO survey for a given year (files are configured in a structure specified for use with the tool)
➢   determine thermal and dissolved oxygen profiles, and estimate depth of the upper hypolimnion (UHY) for each station visit
➢   display the thermal and dissolved oxygen profiles, and depth of the UHY for each station visit as determined by the tool
➢   the user evaluates depth of the UHY as determined by the tool and either continues with the calculation of oxygen depletion rate or can select different depths for the UHY based on the thermal and dissolved oxygen profiles. This option is especially critical for atypical profiles.
➢   calculate the oxygen depletion rate based on Rosa and Burns (1987) including adjusting for vertical mixing, hypolimnion thickness, and seasonal variability
➢   calculate the corrected oxygen depletion rate for each station
➢   calculate the mean oxygen depletion rate for all stations
➢   output the oxygen depletion rate for the Central Basin of Lake Erie for a given year

2.0   Installation

The Lake Erie Oxygen Depletion-Rate Calculation Tool comes packaged on an installation CD-ROM so that it will automatically install itself when the setup program is run. Follow the steps below to install the tool on your computer.

·   Insert the Lake Erie Oxygen Depletion-Rate Calculation Tool CD-ROM in your CD-ROM Drive.

·   Select the Windows "Start" button.

·   Select "Run..."

·   Either browse to your CD-ROM drive and select setup.exe or type in the drive letter of your CD-ROM drive followed by setup.exe, (e.g.,D:\setup.exe) then click on "OK."

·   Follow the instructions that appear on your screen.

To complete the installation, users will be required to edit the Windows Registry on their machines before the Tool can process the larger SeaBird data files. Some of the larger files have in excess of 30,000 records (i.e., rows of data).

Microsoft Access has a default editing limit of 9500 records in a single processing step. More records can be edited in a single step by increasing the value of the "MaxLocksPerFile" entry in the Windows Registry. The "MaxLocksPerFile" entry can be edited by following the steps outlined below:

·   Select the Windows "Start" button

·   Select "Run..."

·   Type "regedit" in the text box labeled "Open"

·   Browse to MY COMPUTER\HKEY_LOCAL_MACHINE\Software\Microsoft\Jet\ 4.0\Engines\Jet 4.0

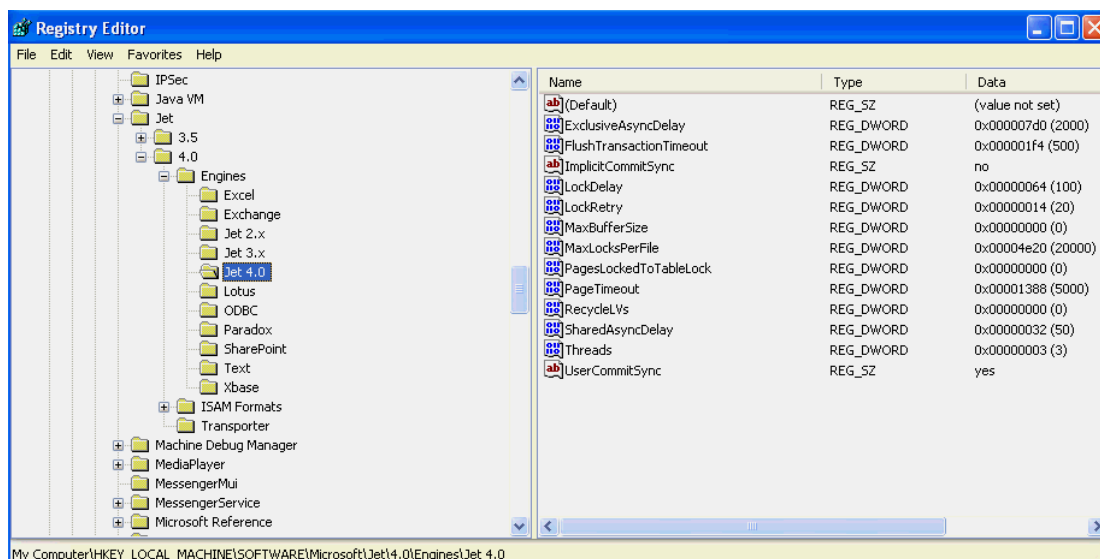The window open on your screen should look like the one below, Figure 1.

Figure 1. Registry Editor

If you double click on the "MaxLocksPerFile" located in the right hand side of your current window, a window like the one shown below (Figure 2) opens.
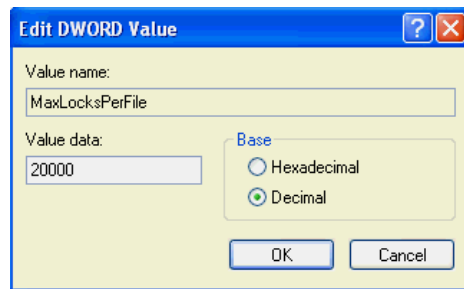
Figure 2. MaxLocksPerFile Adjustment Window

Click on the radio button labeled "Decimal" and the current value of MaxLocksPerFile will be displayed in the text box labeled "Value data:" Changing the value to at least 20,000 should allow the tool to process most data files. The largest editing step the tool performs is an initial one where the data are coded as upcast or downcast data. Since the data are coded as downcast by default when imported, only half of the database will have to be edited (i.e., a 20,000 MaxLocksPerFile will allow editing a data set containing approximately 40,000 records).

3.0   Using The DO Depletion Tool

Operation of the tool is divided into three parts. The first part involves the tool importing temperature and dissolved oxygen data from text files generated from the SeaBird or other comparable software. Imported data are automatically processed through an algorithm that provides an initial estimate of the Upper Hypolimnion (UHY), and average temperature and DO values for the water layers above and below the UHY. The second part involves the user's evaluation and acceptance of the estimated UHY for that visit at that station. Finally, once the data have been imported and accepted for all visits at all stations within a given year, the tool calculates a time-weighted oxygen depletion rate for the season.

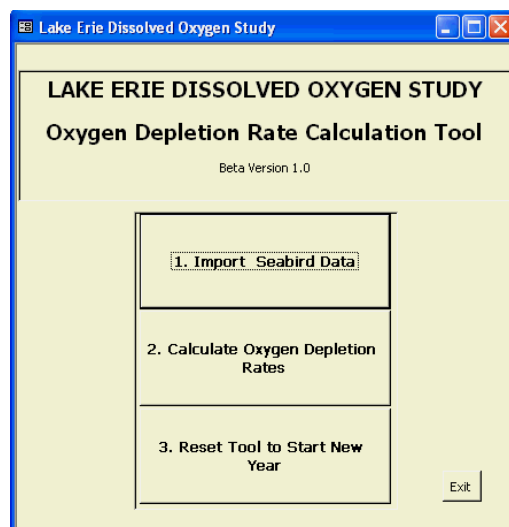The opening screen of the DO Depletion Tool is shown in Figure 3.

Figure 3. Opening Screen

3.1   Importing Data

The first step in operating the tool is to import the text files that contain the temperature and dissolved oxygen data for each visit at each station. The import screen can be accessed by selecting "Import SeaBird Data" on the opening screen. The form shown in Figure 4 will open next.

Figure 4. Import Screen

Input files for the oxygen depletion rate calculation tool can be prepared with the aid of SeaBird Data Processing software or any other application capable of generating ASCII files. A detailed discussion on the preparation of input files can be found in Appendix D. After the input files have been created according to the instructions in Appendix D, the user needs to browse to or type in the name of one of the input files along with its associated drive and full path in the upper left hand corner of the screen in the "Import File" field, (e.g., E:\2003 August 19-20\er37.txt) and select "Import SeaBird Data." The user will notice that when Canadian data are imported, station number and date information will need to be entered. The station number must be entered in the following format: ERXX, where XX corresponds to the 2-digit station number.

The tool will import the data specified by the user, process the data through an algorithm, and provide an estimate of the UHY.

3.2   Data Evaluation

Once the data have been imported, graphs of both temperature and dissolved oxygen profiles are available for the user to evaluate the initial estimate of the UHY. If the user agrees with the tool's estimate of the UHY,

selecting the "Accept Calculations" button will add the data for that visit at that station to the database that will be used to calculate the overall oxygen depletion rate.

If the user feels the tool's estimate of the UHY needs to be adjusted, the user can enter a revised UHY estimate in the text box (half way down the left side of the form just to the right of the label stating "Final UHY (m)") and then select the "Recalculate" button. The tool will recalculate the temperatures, dissolved oxygen, and hypolimnion thickness associated with the revised UHY. If the user agrees with the revised UHY and its associated temperatures and DOs, the user should select the "Accept Calculations" button and import data for the next visit.

To aid in deciding whether the UHY should be adjusted, the tool provides several warning messages that signal that the estimation algorithm may not have been successful, or that the given station visit may not be appropriate for use in calculating the DO depletion rate. These warning messages are listed below. For more details on the UHY estimation algorithm, see Appendices A and C.

"Caution: Algorithm did not converge on a single UHY value." - This states that the recursive algorithm did not converge to a single depth. In this case, the value listed as the final UHY is merely the result occurring in the last iteration, and should not be used.

"Caution: Maximum and minimum temperatures are less than one degree apart." - This states that the range between the minimum and maximum temperatures observed differed by less than one degree, and therefore the lake may have been isothermal and no UHY would exist.

"Caution: Positive metalimnion slope." - This states that, based on the depth range the algorithm selected to represent the metalimnion, the temperature increases as depth increases. This will likely occur if the algorithm defined the metalimnion incorrectly, or that the lake may be isothermal. The user should examine the graphs to determine whether the estimated UHY should be used.

"Caution: Anomalous Hypolimnion slope" - This states that, based on the depth range the algorithm selected to represent the hypolimnion, the temperature is either strongly increasing or decreasing as depth increases. Specifically, the estimated hypolimnion slope is either greater than 2 or less than -2. This will likely occur if the algorithm defined the metalimnion and hypolimnion incorrectly. The user should examine the graphs to determine whether the estimated UHY should be used.

"Caution: Hypolimnion thickness is less than 1 meter" - This states that the estimated UHY is less than one meter above the lowest depth that temperature measurements were taken. While the bottom depth is later increased by a level specified by the user (typically one meter), and therefore the final hypolimnion thickness will always be greater than the originally estimated amount, the number of measurements available to estimate the hypolimnion slope will be small when this warning appears. Therefore, the user should examine the graphs to determine whether the estimated UHY should be used.

"Caution: Upper Hypolimnion estimated to be <10 meters from surface" - Because the depth of the lake at the sampling stations is greater than 20 meters, it is unlikely that the upper hypolimnion will be less than 10 meters from the surface. Therefore, it is likely that the algorithm defined the metalimnion incorrectly, or that

the lake may be isothermal when this warning occurs. The user should examine the graphs to determine
whether the estimated UHY should be used.

"Caution: Metalimnion > 10 meters wide" - This occurs when the initial estimates of the UHY and LEP are
apart by more than 10 meters. Because this is not likely to occur, it is likely that the algorithm defined the
metalimnion incorrectly, or that the lake may be isothermal when this warning occurs. The user should
examine the graphs to determine whether the estimated UHY should be used.

Please note that the presence of these warning messages (other than the message about the algorithm not
converging) do not always indicate that the estimated UHY is inappropriate. Therefore, it is imperative that the
user review the graphs prior to making any decisions.

It is important to note that the tool will only accept one set of data for each visit at each station. To view the
data accepted by the tool for each visit at each station, the user should select "View Processed Profiles" button
on the bottom of the form. A form like the one shown in Figure 5 will open.

	Include	Isothermal	Station	UpLoadDate	Oe	Oh	Te	Th	thick	Julian
▶	☑	☐	ER42	7/17/2002 11:08:03 PM	9.22	5.58	21.01	10.29	2.994	77
	☑	☐	ER38	7/18/2002 6:35:04 AM	9.71	7.00	21.20	11.23	3.416	78
	☑	☐	ER36	7/18/2002 6:35:04 AM	9.71	7.00	21.20	11.23	3.416	78
	☑	☐	ER30	7/18/2002 2:18:04 PM	9.21	7.35	20.81	10.01	4.477	78
	☑	☐	ER31	7/18/2002 4:56:02 PM	9.70	8.37	21.35	11.08	5.566	78
	☑	☐	ER32	7/18/2002 7:44:01 PM	9.43	8.52	21.15	10.98	4.716	78
	☑	☐	ER43	8/6/2002 10:28:00 PM	8.59	3.09	23.69	11.96	4.082	97
	☑	☐	ER42	8/7/2002 12:31:01 AM	8.65	2.13	23.48	12.30	3.168	98
	☑	☐	ER73	8/7/2002 2:17:05 AM	8.50	4.38	23.47	10.98	5.245	98
	☑	☐	ER36	8/7/2002 4:03:02 AM	8.70	4.81	23.35	11.81	4.533	98
	☑	☐	ER37	8/7/2002 5:37:01 AM	8.41	4.17	23.45	11.16	3.856	98
	☑	☐	ER38	8/7/2002 7:50:04 AM	8.75	2.83	23.52	11.76	4.427	98
	☑	☐	ER30	8/7/2002 10:19:04 AM	8.09	4.92	21.40	10.34	4.772	98
	☑	☐	ER31	8/7/2002 11:51:03 AM	9.22	5.09	22.73	11.31	5.284	98
	☑	☐	ER78	8/7/2002 1:22:05 PM	8.35	5.11	22.89	12.05	3.57	98
	☑	☐	ER32	8/7/2002 3:44:01 PM	8.37	5.31	23.06	12.02	5.162	98
	☑	☐	er32	8/28/2002 12:26:05 PM	7.00	2.95	22.93	13.48	2.834	119
	☑	☐	er78	8/28/2002 2:13:02 PM	7.27	2.48	23.09	11.87	4.668	119
	☑	☐	er38	8/28/2002 5:05:01 PM	7.17	2.12	21.71	11.01	5.995	119
	☑	☐	er30	8/29/2002 9:27:02 AM	6.89	6.36	22.69	13.24	2.737	120
	☑	☐	ER31	8/29/2002 11:11:05 AM	8.24	1.22	22.74	13.61	1.773	120
	☑	☐	er37	8/29/2002 2:43:00 PM	8.35	1.40	23.00	11.73	5.827	120

Record: ◀◀ ◀ 1 ▶ ▶▶ ▶✳ of 26

Figure 5. Processed Temperature and Dissolved Oxygen Profile Data

If for some reason the user does not want the data for a visit to be included in the overall oxygen depletion rate
calculation, the user can uncheck the check box associated with that visit and the tool will not include the data
in the overall oxygen depletion rate calculation. If the user wants to delete all the data for a visit, they must
highlight the row that contains the information they want deleted by clicking on the very left most rectangular
box where the record pointer is and select delete from their keyboard.

The tool has an additional check box used to signify any station visits that appeared to be isothermal. The user
should make this judgment based on the depth profile and any warning messages that appeared during the UHY
estimation algorithm. Please note that the temperature range and other warning messages will not immediately
cause the box to be checked; this must be done by the user. Also, note that the "Accept Calculations" button
must be pressed for any isothermal stations to appear in the summary sheet; however the user likely want to

uncheck the "Include" check box for any isothermal visits so they are not included in the depletion rate calculation.

Important Note: The tool has a built-in quality control that prevents it from accepting two sets of data from a station with the same upload date. However, some cruises have been noted to have multiple data sets (A and B, 1 and 2, etc.) for a single cruise at a station. These sets will have separate upload dates/times and can both be accepted by the tool. These data sets can be compared for the purposes of determining which of the two is more appropriate for interval calculation or as a consistency check. However, the tool cannot utilize both data sets properly for interval calculations. Therefore the tool will warn the user when they have attempted to calculate intervals containing multiple data sets from the same date. The tool will automatically direct the user to the processed profiles screen where the user must uncheck or delete one set of the data from the same date to continue.

3.3   Calculation of Oxygen Depletion Rates

Once all of the temperature and dissolved oxygen data have been processed for all station visits of interest, the overall oxygen depletion rate can be calculated. The form to request the calculation can be accessed from the button on the opening form labeled "Calculate Oxygen Depletion Rates" (see Figure 3), or from the import screen by selecting the button labeled "Open Calc Form" (Figure 4). Once either button is selected, the following form (Figure 6) opens.
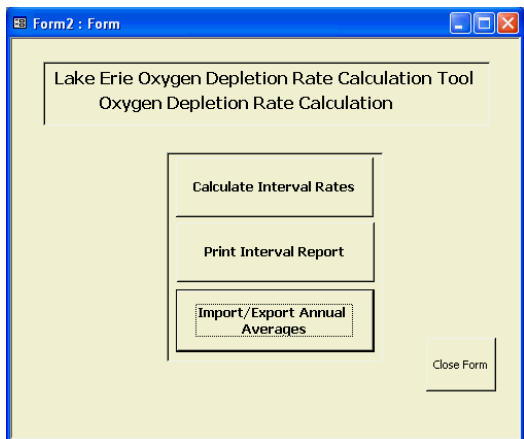
Figure 6. Oxygen Depletion Calculation Form

Selecting the button labeled "Calculate Interval Rates" requests the tool to calculate the oxygen depletion rates for each interval of time between visits for each station visited. Once calculated a form like the one shown in Figure 7 opens.

Figure 7. Calculated Interval Data

In cases where data are not available for either the beginning of an interval or the end of an interval for a station, the system inserts a null code of -999. This null code of -999 will not be included any oxygen depletion rate calculations.

If the user selects "Print Interval Report" from the calculation screen, a report like the one shown in Figure 8 is generated and is available to print.
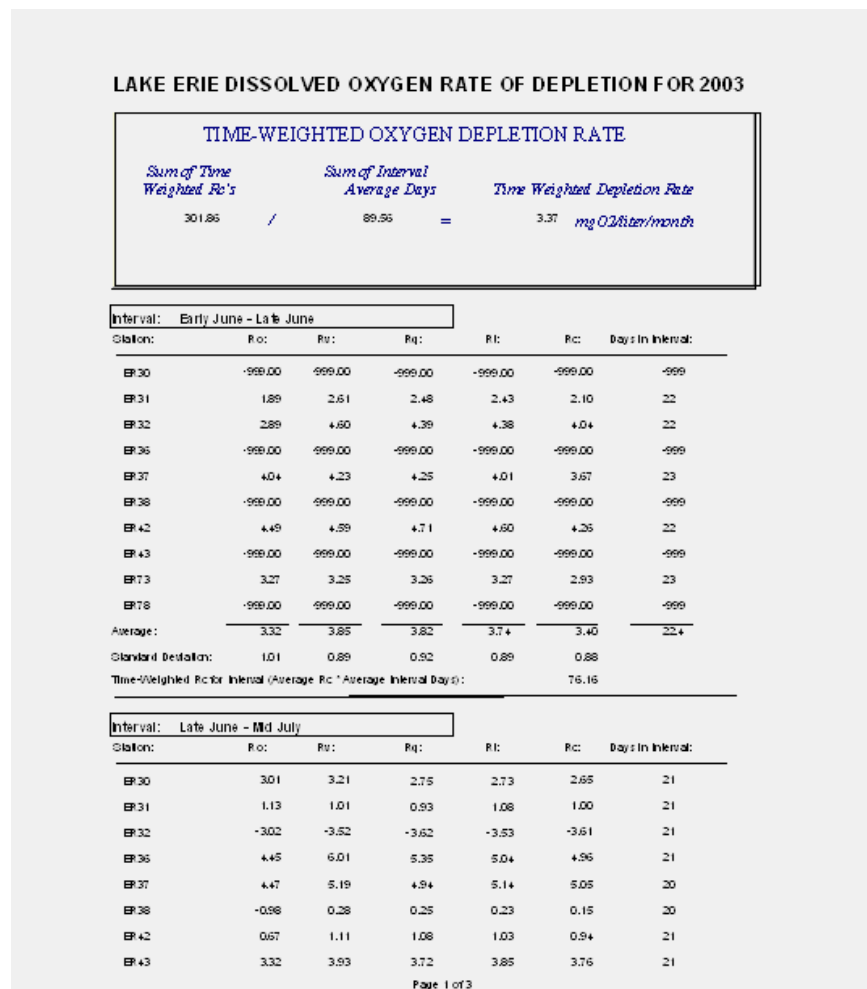
Figure 8. Example Final Report

Data sets generated each year can now be saved with the "Import/Export Annual Averages" button on the Oxygen Depletion Calculation Form. When the "Import/Export Annual Averages" button is selected a form like the one shown below opens.

Data that are exported are the average DO and temperature data shown in Figure 5. The data can be saved, and re-imported back into the tool at a later date for additional analysis if necessary.

**APPENDIX A: LAKE ERIE OXYGEN DEPLETION RATE CALCULATION TOOL STEP-BY-STEP
PROCEDURE FOR AUTOMATED THERMAL STRUCTURE ESTIMATION SCHEME**

The following draft procedure is used to estimate the upper hypolimnion (UHY) depth based on the data generated from the SeaBird CTD for use in calculating oxygen depletion rates in Lake Erie. Once this estimated depth is determined, the Calculation Tool will provide it to the user for validation. The user can choose to use the depth estimated by the tool or enter a specific depth for the UHY as determined from review of the temperature depth trace. The tool will then proceed with calculating oxygen depletion rates as described in Rosa and Burns, *Lake Erie central Basin Oxygen Depletion Changes From 1929 to 1980*, J. Great Lakes Res. 13(4):684-696, 1987 and detailed in the 10/90 email from Chip O'Leary.

Part I. Conduct initial estimates of depths for LEP and UHY

In this part, two initial depth estimates are made, approximately encompassing the metalimnion. This is done to assign depths and associated temperature values to the metalimnion and hypolimnion. Depths that are more shallow than the estimated metalimnion are not used in the algorithm. Unweighted linear regression models are then fit for each of the two pieces of data in Part II in order to make an initial estimate of the UHY of the profile.

1.   Calculate mean temperature (for each rounded 0.01m depth)
        The 0.01 m depth is used to minimize the effect of oscillation of depth in the data that may result in exaggeration of temperature differences in the next step
2.   Estimate slope, as absolute value, for each 0.01m, based on the following formula: (temperature - temperature from previous 0.01m) divided by (rounded depth - previous rounded depth)
3.   Calculate mean absolute estimated slope for each 0.1m
4.   Excluding the shallowest 3m and the deepest 1m, Pick two highest Mean Absolute Estimated Slopes.
5.   Divide original data (no rounding, including all depths), into 2 pieces:
        Metalimnion = Depths between 2 points picked in #5
        Hypolimnion = Depths below deeper of 2 points picked in #5

Depths above shallower of 2 points picked in #5 are not assigned to either category

Part II. Calculate first estimate of UHY

In this part, an unweighted linear regression model is fit for each set of data assigned to the metalimnion and hypolimnion. The UHY of the temperature depth trace is then determined.

6.   Fit two unweighted linear regression models for the temperature depth trace of the metalimnion and hypolimnion
7.   Determine the estimated UHY of the temperature trace.
        The UHY is determined by trisecting the angle between the metalimnion and hypolimnion temperature traces. The UHY is the lower 1/3 angle intercept.

Part III. Reiterate

In this part, the depths of the UHY is recalculated by reiterating Part II 10 times and testing for convergence of depth estimation.

Assign original data to the metalimnion and hypolimnion based on results from Part II.

Hypolimnion = Depths below UHY estimated in last iteration

Metalimnion = Same as original (not based on latest upper and lower knees)

Repeat steps in II using re-assigned data

If UHY is not the same as in previous run, repeat III 1) and 2)

If UHY has not converged in 10 reiterations, the UHY cannot be determined

APPENDIX B: DATABASE DATA ELEMENT DICTIONARY

Data Table: tblAveragebyDepth

Field Name	Type	Size	Key	Description
Cast	Text	5		"D" = Downcast Data; "U" = Upcast data
Depth	Number	Double		Depth (m)
AvgOfTemperature	Number	Double		Average of temperature (°C)
AvgOFDO	Number	Double		Average of Dissolved Oxygen (mg/L)

Data Table: tblAverages

Field Name	Type	Size	Key	Description
Depth	Number	Double		Depth (m)
AverageTemperature	Number	Double		Average of temperature (°C)
AverageDO	Number	Double		Average of Dissolved Oxygen (mg/L)
Cast	Text	5		"D" = Downcast Data; "U" = Upcast data

Data Table: tblCalculations

Field Name	Type	Size	Key	Description
Depth	Number	Double		Depth (m)
AvgOFTemperature	Number	Double		Average temperature (°C)
AvgDO	Number	Double		Average Dissolved Oxygen (mg/L)
DeltaDepth	Number	Double		Change in depth from previous record (m)
DeltaTemp	Number	Double		Change in temperature from previous record (°C)
Slope	Number	Double		[Temperature]/[Depth]
DeltaSlope	Number	Double		[DeltaTemp]/[DeltaDepth]

Data Table: tblCalculations2

Field Name	Type	Size	Key	Description
Depth	Number	Double		Depth (m)
AvgOfSlope	Number	Double		Average slope for specified depth
AvgOfDeltsSlope	Number	Double		Average change in slope for specified depth

Data Table: tblCDODR

Field Name	Type	Size	Key	Description
Include	Yes/No			Include in Rosa and Burns equations.
Station	Text	50	Yes	Station Name
UploadDate	Number	Double	Yes	System upload date
Oe	Number	Double		Average DO for upper water layer.
Oh	Number	Double		Average DO for hypolimnion.
Te	Number	Double		Average Temperature for upper water layer.
Th	Number	Double		Average temperature for hypolimnion.
thick	Number	Double		Thickness of hypolimnion.
Julian	Number	Double		Days since May 1st
Week	Number	Long Integer		Numbered week of the year

Data Table: tblChart1

Field Name	Type	Size	Key	Description
AverageTemperature	Number	Double		Average Temperature (°C)
Depth	Number	Double		Average depth (m)
UHY	Number	Double		Upper Hypolimnion

Data Table: tblChart2

Field Name	Type	Size	Key	Description
AverageTemperature	Number	Double		Average Temperature (°C)
Depth	Number	Double		Average depth (m)
UHY	Number	Double		Upper Hypolimnion

Data Table: tblFinal

Field Name	Type	Size	Key	Description
SunofAvgOfJulian	Number	Double		Sum of interval average days
SumofWeighting	Number	Double		Sum of weighted Rc's
FinalDepletionRate	Number	Double		[SumOfWeighting]/[SumofAvgOfJulian]

Data Table: tblHypo_Summations

Field Name	Type	Size	Key	Description
Y	Number	Double		Sum of Hypolimnion [Depth]s in tblImported
X	Number	Double		Sum of Hypolimnion [Temperature]s in tblImported
XY	Number	Double		Sum of Hypolimnion [Depth]*[Temperature] in tblImported
XX	Number	Double		Sum of Hypolimnion Temperature]*[Temperature] in tblImported
n	Number	Double		Count of hypolimnion records

Data Table: tblImported

Field Name	Type	Size	Key	Description
Depth	Number	Double		Depth (m)
Temperature	Number	Double		Temperature (°C)
DO	Number	Double		Dissolved oxygen, mg/L
F4	Text	50		Not used, import artifact.
F5	Text	50		Not used, import artifact.
F6	Text	50		Not used, import artifact.
F7	Text	50		Not used, import artifact.
F8	Text	50		Not used, import artifact.
F9	Text	50		Not used, import artifact.
Cast	Text	5		Downcast coded as "D", Upcast coded as "U".
Epi_Data	Number	Double		Not Used
Meta_Data	Number	Double		Not Used
Hypo_Data	Number	Double		Not Used
SummXY	Number	Double		[Depth]*[Temperature]
SummXX	Number	Double		[Temperature]*[Temperature]
EpiTri_Depth	Number	Double		Corresponding depth of upper knee's trisect line.
EpiTri_Diff	Number	Double		Depth difference between upper knee's trisect line and the thermal profile.
HypoTri_Depth	Number	Double		Corresponding depth of lower knee's trisect line.
HypoTri_Diff	Number	Double		Depth difference between lower knee's trisect line and the thermal profile.

Data Table: tblIntervalData

Field Name	Type	Size	Key	Description
Interval	Text	50		Interval between visits (days)
Station	Text	50		Lake Erie Station Code
Ro	Number	Double		Uncorrected oxygen depletion rate.
Rv	Number	Double		Oxygen depletion rate corrected for vertical mixing.
Rq	Number	Double		Oxygen depletion rate corrected for temperature.
Rt	Number	Double		Oxygen depletion rate corrected for hypolimnion thickness.
Rc	Number	Double		Oxygen depletion rate corrected for seasonal effects.
Julian	Text	50		Days since May 1st
IntervalStart	Text	50		Numbered week of the year.

Data Table: tblMeta_Summations

Field Name	Type	Size	Key	Description
Y	Number	Double		Sum of Hypolimnion [Depth]s in tblImported
X	Number	Double		Sum of Hypolimnion [Temperature]s in tblImported
XY	Number	Double		Sum of Hypolimnion [Depth]*[Temperature] in tblImported
XX	Number	Double		Sum of Hypolimnion Temperature]*[Temperature] in tblImported
n	Number	Double		Count of hypolimnion records

Data Table: tblRawImported

Field Name	Type	Size	Key	Description
Depth	Number	Double		Depth (m)
Temperature	Number	Double		Temperature (°C)
DO	Number	Double		Dissolved oxygen, mg/L
Cast	Text	5		Downcast coded as "D", Upcast coded as "U".
Epi_Data	Number	Double		Not Used
Meta_Data	Number	Double		Not Used
Hypo_Data	Number	Double		Not Used
SummXY	Number	Double		[Depth]*[Temperature]
SummXX	Number	Double		[Temperature]*[Temperature]
EpiTri_Depth	Number	Double		Corresponding depth of upper knee's trisect line.
EpiTri_Diff	Number	Double		Depth difference between upper knee's trisect line and the thermal profile.
HypoTri_Depth	Number	Double		Corresponding depth of lower knee's trisect line.
HypoTri_Diff	Number	Double		Depth difference between lower knee's trisect line and the thermal profile.

Data Table: tblStations

Field Name	Type	Size	Key	Description
Station	Text	50		Lake Erie Station Code
Latitude	Text	50		Latitude
Longitude	Text	50		Longitude

Data Table: tblSystemUploadTime

Field Name	Type	Size	Key	Description
Field1	Text	74		System Upload Date and Time as imported.

Data Table: tblTrips

Field Name	Type	Size	Key	Description
Week	Number	Integer		Numbered week of the year.

Data Table: tblWeelDecode

Field Name	Type	Size	Key	Description
WeekNo	Number	Integer		Week Number
WeekLabel	Text	50		Label for numbered week

Data Table: tblWeighting

Field Name	Type	Size	Key	Description
Interval	Text			Monthly description of interval period (e.g., Late June - Mid July)
AvgOfRc	Number			Average of the oxygen depletion rates corrected for seasonal effects.
StDevOfRc	Number			Standard deviation of the oxygen depletion rates corrected for seasonal effects.
AvgOfJulian	Number	Double		Average of interval days
CountOfRc	Number	Double		Number of Rc's in AvgOfRc
Weighting	Number	Double		[AvgOfRc] * [AvgOfJulian]
LastOfIntervalStart	Text			Last week of interval

Data Table: ttblAverages

Field Name	Type	Size	Key	Description
ID	AutoNumber			AutoNumber
Depth	Number	Double		Depth (m)
AverageTemperature	Number	Double		Average Temperature (°C)
AverageDO	Number	Double		Average Dissolved Oxygen (mg/L)
Cast	Text			"D" = Downcast Data; "U" = Upcast data

Data Table: ttblRounded

Field Name	Type	Size	Key	Description
RoundDepth	Number	Double		Rounded Depth measurement (m)
Temperature	Number	Double		Temperature (°C)
DO	Number	Double		Dissolved oxygen (mg/L)
Cast	Text			"D" = Downcast Data; "U" = Upcast data

APPENDIX C: EXPLANATION OF UHY DETERMINATION ALGORITHM

In order to properly estimate the rate of DO depletion, the Oxygen Depletion Rate Calculation Tool needs to determine an estimate of the depth at which the hypolimnion of Lake Erie begins at the given sampling station. This is done by determining the depth at which the temperature begins to drop rapidly, i.e., the metalimnion. The upper hypolimnion (UHY) is just below this depth, as displayed by the red line in Figure C.1 below. As seen from this figure, the temperature drops off rapidly starting at around 11 meters, levels off at the UHY at approximately 17 meters, and is approximately stable until the bottom depth at the site.
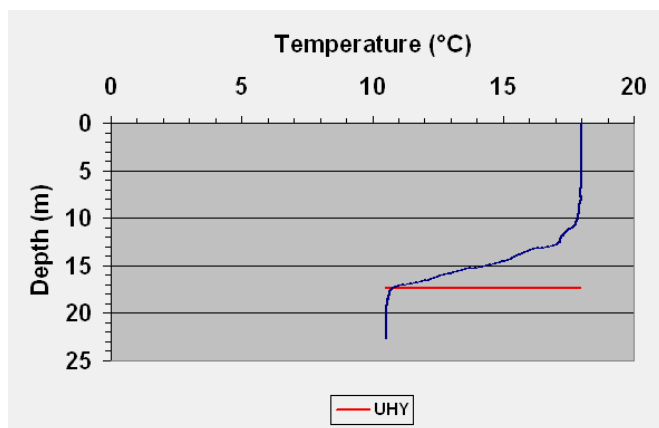
The Rate Calculation Tool determines the UHY through use of a recursive procedure which fits linear regression models on subsets of the depth and temperature results taken in the downcast measurements. The procedure is recursive because it re-categorizes depths as being in the epilimnion or hypolimnion based on the estimated UHY determined in the prior step. In order to do this, an initial estimate of the metalimnion depths must be made. The Rate Calculation Tool does this by picking two depths in the metalimnion, and uses all measurements taken between these depths to fit a least squares regression line approximating the drop in temperature. The two chosen depths do not need to represent the whole range of the metalimnion; the rate of temperature drop should not change much in the metalimnion, so the estimated line should not differ greatly based on the chosen depths as long as they do in fact occur in the metalimnion.

The two depths chosen in the initial estimation of the metalimnion are made by treating the depth profile as a continuous curvilinear function. The derivative of a curvilinear function is the slope of the line tangent to the function at a specified point. By targeting the depth for which the slope is most negative, the metalimnion can be estimated since this is where the temperature drops at the greatest rate. Please note that the Y axis in Figure X is reversed, so the slope of a tangent line at the metalimnion would appear to have a positive slope but would in fact be negative. The Rate Calculation Tool does not directly fit a function to the data, but empirically calculates the slope by calculating the change in temperature between each depth and the depth at which the previous measurement was taken, divided by the difference in depth between the two measurements. The tool then selects the two depths at which the slope is most negative.

Because of the large number of temperature measurements taken, and the variability in depth differences between consecutive measurements, average temperature is calculated for each 0.01 meter, prior to the calculation of the empirical slopes. In addition, rather than selecting the two depths to estimate the metalimnion based on single slope estimates, the empirical slopes are averaged for each 0.1 meter. The selected depths, therefore, are the ones for which the mean slopes are the most negative. The average slopes are used to reduce

the chances that a single unusual measurement will cause the algorithm to select a depth that is not in the metalimnion.

Once the two initial depths are selected, two least squares regression lines are fit. A line approximating the metalimnion is fit using all depth measurements between the two selected depths. A line approximating the hypolimnion is fit using all depth measurements below the deeper of the two selected depths. Based on these two lines, a third line is also fit, based on the trisect. Based on this trisect line, an initial estimate of the UHY is made.

Using the initial UHY estimate, the data are reapportioned, and the hypolimnion line is refit using only depth measurements made below the estimated UHY. The metalimnion line is not refit. The trisect line is determined using the new hypolimnion line, and a new UHY estimate is made. This process repeats 10 times, after which the UHY estimates should converge to a single depth, or to multiple depths within 0.1 meter. In some cases, this will not occur, and the UHY estimates will vary widely between repetitions of the recursive procedure. In this case, it is likely that one or both of the initially chosen depths were not in the metalimnion, and therefore the fitted lines were inappropriate. The Rate Calculation Tool will alert the user that this has occurred, and the user should manually select the UHY based on the graphical display of the data. In other cases, the UHY estimates will converge on a single depth, but this depth may not accurately reflect the UHY. Several warning messages, based on the slopes of the linear regression lines, the distance between the two depths initially selected to estimate the metalimnion, and the depth of the UHY in relation to the depth of the lake, may appear, to alert the user that the estimated UHY is not appropriate. However, these warning messages may occur even though the estimated UHY is appropriate, and examination of the depth profile graph is vital in all cases.

APPENDIX D: PREPARING INPUT FILES FOR THE DO DEPLETION TOOL

Input files for the oxygen depletion rate calculation tool can be prepared with the aid of SeaBird Data
Processing© software or any other application capable of generating ACSII files. If the files are going to be
generated with the aid of the SeaBird software, guidance is provided in Section D.1. If ASCII text files are
going to be generated with other software, guidance is provided in Section D.2.

D.1 Preparing Files from SeaBird Data

Input files for the oxygen depletion rate calculation tool can be prepared with the aid of SBE Data Processing©
software. A copy of the software can be downloaded from SeaBird's website
(http://www.SeaBird.com/software/SBEDataProcforWindows.htm). SBE Data Processing© consists of a
collection of menu-driven routines for converting, editing, processing, and plotting of oceanographic data
acquired with Sea-Bird equipment.

The opening screen of the data conversion module is shown in Figure D.1 below.

Figure D.1. SBD Data Conversion Opening Screen

File Setup
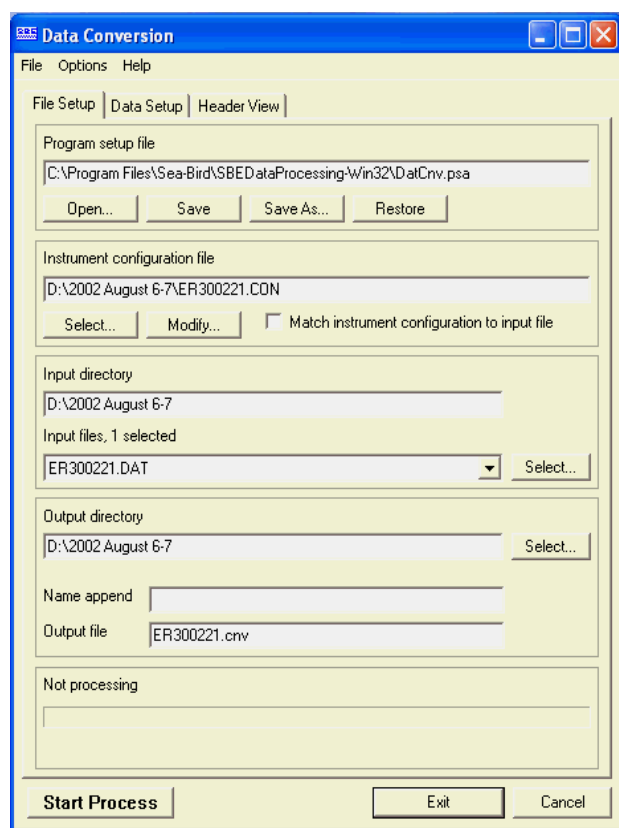
The first step in preparing an input file for the calculation tool is select the "File Setup" tab on the opening screen, as shown in Figure 1. The user should first check the "Instrument Configuration File" shown on the screen. Configuration files have a ".CON" extension are are usually stored with the data files. If the CON file shown is not the correct one, the user will have to click on the "Select..." button and browse to the correct configuration file. Next, the SeaBird module needs to know where the data files are so they can be read into SeaBird. If the data file shown is not the correct one, the user will have to click on the "Select..." button and browse to the correct data file.

Critical: *SeaBird will output the requested data in a text file with a CNV extension. This extension will need to be changed after SeaBird creates the CNV. file. The extension needs to be changed to .txt so Access will recognize that it is importing a text file. If this is not done, the DO Depletion Tool will not recognize the data file format and will not be able to import the data.*

Data Setup

When the file setup screen is complete, the user should click on the "Data Setup" tab. A screen like the one shown in Figure D.2 is displayed. This data setup screen should only need to be configured once. The SeaBird conversion tool remembers the previously entered data. Most of the data are default settings. Some of the settings that do not need to changed are:

· Process scans to end of file: Checked
· Scans to skip over: 0
· Output Format: ASCII
· Convert Data from: Upcast and Downcast
· Create File Types: Create converted data (CNV) file only
· Merge Separate Header File: Not Checked

Finally, SeaBird needs to be told which variables to incorporate into the .CNV file. The user needs to click on the "Select Output Variables" to open a screen like the one shown in Figure D.3.
The data needed by the tool are:

· Depth (fresh water, m)
· Temperature (ITS-90, deg C)
· Oxygen, SBE 43 (mg/l)

The variables shown in Figure D.3 are the parameters needed and they are listed in the order needed to be properly processed by the tool. The parameters can be selected by scrolling up or down the list of parameters on the right hand side of the Select Output Variables screen as shown in Figure D.3. Double clicking on a parameter can open a list of the different units available for the selected parameters. Clicking on the parameter with the proper units will highlight the parameter. Clicking on the "Add" button located in the center of the

screen will add the highlighted parameter to the Variable Name list on the left side of the Variable Output Screen.

One the variables are set, the user should click on the "File Setup" tab and then click on the "Start Process" button. SeaBird will then create a CNV file for the parameters selected in the location specified for the output file directory.
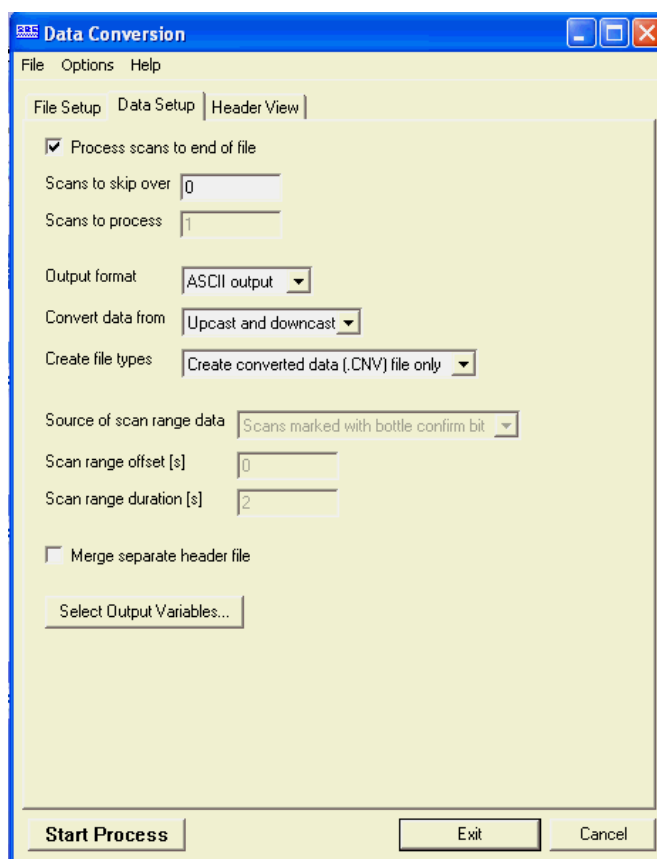
Figure D.2. Data Setup Screen
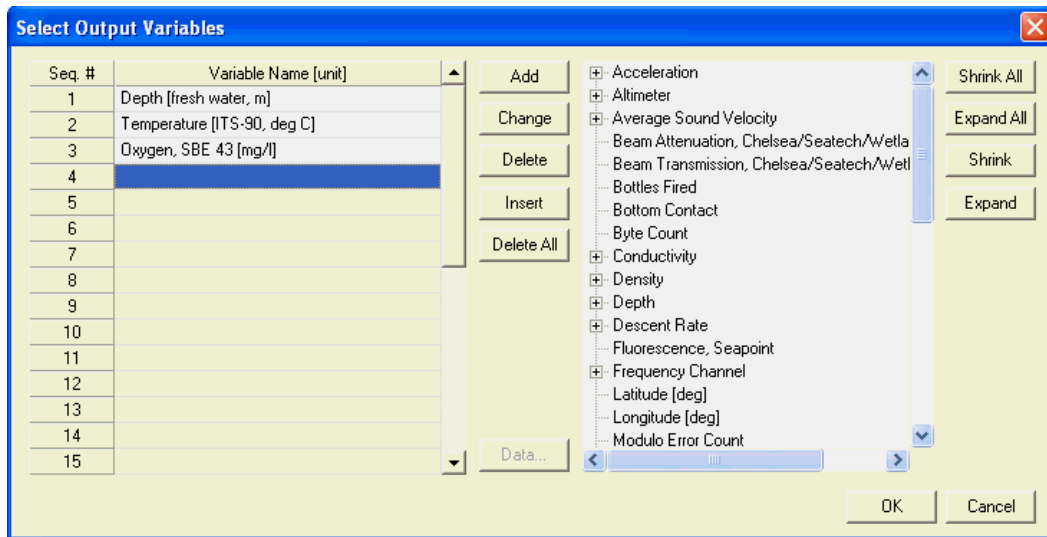
Figure D.3. Select Variables Screen

D.2 Using Data Gathered from Environment Canada

Data are currently being received from Environment Canada in two different file formats (*.S4A and *.dat files). The *.S4A files contain bin averaged down-cast data averaged to 0.5 meters and the profiles are adjusted for the time delay of the O_2 sensor (unknown delay). The *.DAT files are down-cast data as well, however they are not bin averaged or adjusted for any delay in O_2 readings.

The import screen has a type field that has to be set for the type of data being imported. The three choices are:

1. Upcast and Downcast Data
2. Down Cast Data Only (.DAT Files), or
3. Down Cast Data Only (.S4A Files)

It is important to note that when data from Environment Canada are being imported, the user must also provide a **Station** name and **System Upload Date**. The station number must be entered in the following format: ERXX, where XX corresponds to the 2-digit station number. The user will probably have to refer to a cross reference sheet to decode the Canadian station names and dates into those comparable with the SeaBird data files. Station names and system upload dates automatically are read into the system when SeaBird data files are imported.

Importing *.S4A Files

Two things have to be modified in the S4A file before they can be processed. First, lines 6 through 14 of the file header have to be deleted. These lines contain numeric information that could be confused as temperature and DO data. The first five lines of data contain quote marks and this data will come in as text strings and will not be confused with numeric data. Secondly, the file extension need to be changed to .TXT so that the Access import method can recognize the file as an ASCII text file.

Also it is important to remember to fill in the "Station" and "System Upload Date" fields when importing Canadian data. The user will probably need a cross reference sheet to identify the standard GLNPO station names (e.g., ER30, ER32, etc.) and the sampling dates.

File 0980337.S4A

```
          "0980337.S4D""DP""LAKE ERIE""LIMNOS""2004-01-013""33/0980/33"
          "2004-08""18-1523""42-07-01""081-14-59""23.1"" 991.82"
          " O2 RECAL'D  CAL OK GOOD PROFILE"
          "107"" 220288"" 1041"" 290211"
          " 341"" 41026"" 220288"
Delete=>  .000010527 -.0000000021053  6.3789 -1.86  .0997
Delete=>  -.033  .85  .00015  2 -.0049
Delete=>  1000  .00478532683  .000694999306  .0000391659352  .0000043408193
Delete=>  524.5775 -.138284  .00000007269956
Delete=>  20.3495  0  .25  660
Delete=>  4.2 -.000974427013  .580886694 -4.23472861 -.0000667624216  .02
Delete=>  4.68  2.4824
Delete=>  1030.7  1880  7641.7825  3699  3692.0001  2788.8012  3013.3
Delete=>  10.39039  .11359  91.73425  206  0  0


              10.04   21.46   0.00   80   280 99.00   35
              10.06   21.46   0.50   80   280 99.00   71
              10.09   21.46   1.00   80   280 99.00   78
```

Importing *.DAT Files

When importing *.DAT files from Environment Canada type field on the import screen has to be set for "Down Cast Data Only (.S4A Files)." It is also important to note that the user must also provide a **Station** name and **System Upload Date**. The user will probably have to refer to a cross reference sheet to decode the Canadian station names and dates into those comparable with the SeaBird data files. Station names and system upload dates automatically are read into the system when SeaBird data files are imported.

D.3 Alternate Data File Specifications

If an ASCII input file is to be created without the aid of the SeaBird Data Conversion Module, the following information describes the required format of an input data file. The required format consists of two different line formats: a header line format and a data line format.

Header Line - The SeaBird Data Conversion Module creates 45 lines of header information and Access uses only one of them. An example of the one required header line is as follows:

* System upload Time = Aug 19 2003 18:46:18

Line positions 1 through 22 need to read as "* System upload Time = ". Access takes the data from line position 23 to the end of the line and converts it into a date and time data element. This is the date that Access assigns to the data that follow. Acceptable alternative date formats are as follows:

- 8/19/2003 6:46:18 PM
- 19-Aug-03 18:46
- August 19, 2003 6:46 PM

Data Line - All data lines should be of the same format. The data line must consist of the same data elements in the same order. The specifications for the data line are:

Line Position	Data Element	Format
1 – 11	Depth, (m)	11 positions, numeric with decimal point and 3 decimal places
12 – 22	Temperature, (°C)	11 positions, numeric with decimal point and 4 decimal places
23 – 33	Dissolved Oxygen, (mg/L)	11 positions, numeric with decimal point and 5 decimal places

Note: The total number of decimal places are not critical as long as the total number of positions, including the decimal point, does not exceed 11 for any of the data elements.

File Name - The requirements for naming each file are as follows:

·   The first two positions of the filename must begin with "er" (either upper or lower case)

·   Positions 3 and 4 must be one of the ten coded stations (i.e., 30, 31, 32, 36, 37, 38, 42, 43, 73, or 78)

·   File names can be greater than four characters, the first four are reserved as discussed above, and blank spaces should be avoided

·   The extension name must be ".txt"

Example Input Data File

Example File Name : er30.txt

Line Position

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	313233

Example Header Line

*		S	y	s	t	e	m		U	p	l	o	a	d		T	i	m	e		=		8	/	1	9	/	2	0	0 3

Example Data Line (Depth, m)   (Temperature, °C)   (Dissolved Oxygen, mg/L)

					0	.	1	3	0				1	2	.	8	1	6	2				8	.	3	4	949

**APPENDIX E: NOTES ON CALCULATION OF VARIABLE
INPUT FOR THE ROSA AND BURNS EQUATIONS**

The tool uses all the data available, however the actual calculation of temperature and dissolved oxygen (DO) variables used in the Rosa and Burns equations are actually derived from tenth-of-meter averages created from all available data. This was in part due to the Access constraint of having less than 3,000 data points when graphing.

Initial Cleanup

Initially, the tool performs two data cleanup steps before averages are calculated. First, to cleanup the highly variable data in the first two meters of data of both the upcast and downcast, the tool deletes the temperature and dissolved oxygen data for the top two meters of data. Averages are calculated for temperature and DO for meters 3 through 4 of both the upcast and downcast. The average values are inserted back into the database for each tenth-of meter values that were deleted.

Secondly, data are routinely missing from the maximum depth the probe travels to the bottom of the lake. Average DO data for the last meter from the upcast are used when available to create tenth-of meter averages for the missing data when possible. Average temperature data for the last meter from the down are used when available to create tenth-of meter averages for the missing temperature data when possible.

Calculation of Input Variables

First, the depths for all available data are rounded to the nearest one tenth of a meter. Next, the temperature and DO data are averaged for each tenth-of-meter for both the upcast and downcast when available. The following variables are estimated from the tenth-of-meter averages.

Mean Hypolimnion DO =   Average of DO data where depth is greater than estimated UHY and cast = 'U.' The exception being when Canadian data are used and the cast = 'D.'

Mean Hypolimnion Temp = Average of temperature data where depth is greater than estimated UHY and cast = 'D.'

Hypolimnion Thickness =   Initial maximum depth + depth-to-bottom specified by the user - final UHY

Mean DO Above UHY =   Average of DO data where depth is less than estimated UHY and cast = 'D.'

Mean Temp. Above UHY = Average of temp data where depth is less than estimated UHY and cast = 'D.'

ATTACHMENT A – EXTRAPOLATED OXYGEN SOLUBILITY IN WATER, BY INCREMENTS OF 1 AND 0.1 DEGREE CELSIUS

Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius

0 to 10 °C, by 1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
0	14.62	1	14.22	2	13.83	3	13.46	4	13.11	5	12.77	6	12.45	7	12.14	8	11.84	9	11.56
1	14.22	2	13.83	3	13.46	4	13.11	5	12.77	6	12.45	7	12.14	8	11.84	9	11.56	10	11.29

0 to 10 °C, by 0.1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
0.0	14.62	1.0	14.22	2.0	13.83	3.0	13.46	4.0	13.11	5.0	12.77	6.0	12.45	7.0	12.14	8.0	11.84	9.0	11.56
0.1	14.58	1.1	14.18	2.1	13.79	3.1	13.43	4.1	13.08	5.1	12.74	6.1	12.42	7.1	12.11	8.1	11.81	9.1	11.53
0.2	14.54	1.2	14.14	2.2	13.76	3.2	13.39	4.2	13.04	5.2	12.71	6.2	12.39	7.2	12.08	8.2	11.78	9.2	11.51
0.3	14.50	1.3	14.10	2.3	13.72	3.3	13.36	4.3	13.01	5.3	12.67	6.3	12.36	7.3	12.05	8.3	11.76	9.3	11.48

Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
0.4	14.46	1.4	14.06	2.4	13.68	3.4	13.32	4.4	12.97	5.4	12.64	6.4	12.33	7.4	12.02	8.4	11.73	9.4	11.45
0.5	14.42	1.5	14.03	2.5	13.65	3.5	13.29	4.5	12.94	5.5	12.61	6.5	12.30	7.5	11.99	8.5	11.70	9.5	11.43
0.6	14.38	1.6	13.99	2.6	13.61	3.6	13.25	4.6	12.91	5.6	12.58	6.6	12.26	7.6	11.96	8.6	11.67	9.6	11.40
0.7	14.34	1.7	13.95	2.7	13.57	3.7	13.22	4.7	12.87	5.7	12.55	6.7	12.23	7.7	11.93	8.7	11.64	9.7	11.37
0.8	14.30	1.8	13.91	2.8	13.53	3.8	13.18	4.8	12.84	5.8	12.51	6.8	12.20	7.8	11.90	8.8	11.62	9.8	11.34
0.9	14.26	1.9	13.87	2.9	13.50	3.9	13.15	4.9	12.80	5.9	12.48	6.9	12.17	7.9	11.87	8.9	11.59	9.9	11.32
1.0	14.22	2.0	13.83	3.0	13.46	4.0	13.11	5.0	12.77	6.0	12.45	7.0	12.14	8.0	11.84	9.0	11.56	10.0	11.29

10 to 20 °C, by 1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO

Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius

10	11.29	11	11.03	12	10.78	13	10.54	14	10.31	15	10.08	16	9.87	17	9.66	18	9.47	19	9.28

11	11.03	12	10.78	13	10.54	14	10.31	15	10.08	16	9.87	17	9.66	18	9.47	19	9.28	20	9.09

10 to 20 °C, by 0.1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
10.0	11.29	11.0	11.03	12.0	10.78	13.0	10.54	14.0	10.31	15.0	10.08	16.0	9.87	17.0	9.66	18.0	9.47	19.0	9.28
10.1	11.26	11.1	11.01	12.1	10.76	13.1	10.52	14.1	10.29	15.1	10.06	16.1	9.85	17.1	9.64	18.1	9.45	19.1	9.26
10.2	11.24	11.2	10.98	12.2	10.73	13.2	10.49	14.2	10.26	15.2	10.04	16.2	9.83	17.2	9.62	18.2	9.43	19.2	9.24
10.3	11.21	11.3	10.96	12.3	10.71	13.3	10.47	14.3	10.24	15.3	10.02	16.3	9.81	17.3	9.60	18.3	9.41	19.3	9.22
10.4	11.19	11.4	10.93	12.4	10.68	13.4	10.45	14.4	10.22	15.4	10.00	16.4	9.79	17.4	9.58	18.4	9.39	19.4	9.20
10.5	11.16	11.5	10.91	12.5	10.66	13.5	10.43	14.5	10.20	15.5	9.98	16.5	9.77	17.5	9.57	18.5	9.38	19.5	9.19

Extrapolated Oxygen Solubility in Water, by Increments of 1 and 0.1 Degree Celsius

10.6	11.13	11.6	10.88	12.6	10.64	13.6	10.40	14.6	10.17	15.6	9.95	16.6	9.74	17.6	9.55	18.6	9.36	19.6	9.17
10.7	11.11	11.7	10.86	12.7	10.61	13.7	10.38	14.7	10.15	15.7	9.93	16.7	9.72	17.7	9.53	18.7	9.34	19.7	9.15
10.8	11.08	11.8	10.83	12.8	10.59	13.8	10.36	14.8	10.13	15.8	9.91	16.8	9.70	17.8	9.51	18.8	9.32	19.8	9.13
10.9	11.06	11.9	10.81	12.9	10.56	13.9	10.33	14.9	10.10	15.9	9.89	16.9	9.68	17.9	9.49	18.9	9.30	19.9	9.11
11.0	11.03	12.0	10.78	13.0	10.54	14.0	10.31	15.0	10.08	16.0	9.87	17.0	9.66	18.0	9.47	19.0	9.28	20.0	9.09

20 to 29 °C, by 1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
20	9.09	21	8.91	22	8.74	23	8.58	24	8.42	25	8.26	26	8.11	27	7.97	28	7.83
21	8.91	22	8.74	23	8.58	24	8.42	25	8.26	26	8.11	27	7.97	28	7.83	29	7.69

20 to 29 °C, by 0.1 °C Increments

T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO	T°C	DO
20.0	9.09	21.0	8.91	22.0	8.74	23.0	8.58	24.0	8.42	25.0	8.26	26.0	8.11	27.0	7.97	28.0	7.83
20.1	9.07	21.1	8.89	22.1	8.72	23.1	8.56	24.1	8.40	25.1	8.24	26.1	8.10	27.1	7.96	28.1	7.82
20.2	9.05	21.2	8.88	22.2	8.71	23.2	8.55	24.2	8.39	25.2	8.23	26.2	8.08	27.2	7.94	28.2	7.80
20.3	9.04	21.3	8.86	22.3	8.69	23.3	8.53	24.3	8.37	25.3	8.21	26.3	8.07	27.3	7.93	28.3	7.79
20.4	9.02	21.4	8.84	22.4	8.68	23.4	8.52	24.4	8.36	25.4	8.20	26.4	8.05	27.4	7.91	28.4	7.77

20 to 29 °C, by 1 °C Increments

20.5	9.00	21.5	8.83	22.5	8.66	23.5	8.50	24.5	8.34	25.5	8.19	26.5	8.04	27.5	7.90	28.5	7.76
20.6	8.98	21.6	8.81	22.6	8.64	23.6	8.48	24.6	8.32	25.6	8.17	26.6	8.03	27.6	7.89	28.6	7.75
20.7	8.96	21.7	8.79	22.7	8.63	23.7	8.47	24.7	8.31	25.7	8.16	26.7	8.01	27.7	7.87	28.7	7.73
20.8	8.95	21.8	8.77	22.8	8.61	23.8	8.45	24.8	8.29	25.8	8.14	26.8	8.00	27.8	7.86	28.8	7.72
20.9	8.93	21.9	8.76	22.9	8.60	23.9	8.44	24.9	8.28	25.9	8.13	26.9	7.98	27.9	7.84	28.9	7.70
21.0	8.91	22.0	8.74	23.0	8.58	24.0	8.42	25.0	8.26	26.0	8.11	27.0	7.97	28.0	7.83	29.0	7.69